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Extensive development of research in radiochemistry all over the world is stimulated by the steadily growing use of atomic power, by the rapidly increasing production of fissionable materials and by the successful application of radioactive isotopes in different fields of science and technology.

In this country a vast program for the construction of electric stations on atomic power is being carried into effect. According to the seven-year plan for the development of national economy in 1959-1965 the industrial use of atomic energy is to be extended considerably. And the chemistry of radioactive elements has been an intensively studied field, too.

[In fact, the investigation of radioactive substances has been a tradition with Russian science. It was begun soon after the discovery of radioactive phenomena and received special impetus in the forties of this century, when the new practical possibilities opened up by the fission of uranium became evident.]

Early in 1958 [the author of this paper] had a privilege to report to the American Atomic Congress in Chicago on the [status] of radiochemical research in the USSR (1). The present review contains information about the most important results of Soviet work on radiochemistry carried out in 1958-1960.

2.
Cocrystallization and adsorption remain very important processes when radioactive elements are isolated from dilute solutions.

As established by Khlopin and his school ^{in USSR} (2, 3, 4), the distribution of microscopic quantities of an isomorphous substance between the solid crystalline and liquid phases obeys the following law:

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$$\frac{x}{(1-x)} \cdot \frac{(1-y)}{y} = D,$$

where x and $(1-x)$ are microcomponent ratios in the solid and liquid medium; y and $(1-y)$ are the respective macrocomponent ratios; D is the fractionation coefficient. In other words, van't Hoff's theory for dilute solutions is applicable to the case where isomorphous mixtures representing dilute solid solutions are formed. In this case the distribution of an electrolyte in a state of extreme dilution between the solid crystalline phase and the liquid phase is analogous to the distribution of a dissolved substance between two immiscible liquid solvents, which is known to obey Berthelot-Nernst law.

7 The fractionation coefficient, D , is a constant value [quantity], independent of either the microcomponent concentration in the solution or the amount of solid phase liberated from the latter, provided that the precipitate and the solution are in equilibrium and that the chemical compounds present in the liquid and solid phases have the same composition.

What has been just stated here has been confirmed by a thorough study of more than 30 systems of true isomorphous substances, viz., $\text{BaCl}_2\text{-RaCl}_2\text{-H}_2\text{O}$; $\text{Ba}(\text{NO}_3)_2\text{-Ra}(\text{NO}_3)_2\text{-H}_2\text{O}$; $\text{Ba}(\text{NO}_3)_2\text{-Ra}(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$; $\text{BaCrO}_4\text{-RaCrO}_4\text{-H}_2\text{O}$; $\text{U}(\text{SO}_4)_2\text{-UX}_1(\text{SO}_4)_2\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$; $\text{Na}_2\text{Te-Na}_2\text{Po-H}_2\text{O}$ and others.

For the isomorphism of second kind (Grimm's mixed crystals) the lower limit of miscibility has been established: the microcomponent begins entering the macrocomponent crystals if its concentration attains a certain minimum (above 10^{-5} - $10^{-6}\%$) sufficient for the microcomponent to build its own crystal lattice. In this case ^{it was proposed} the isolated crystals have a mosaic structure. The existence of a lower miscibility limit has been borne out by the results obtained in investigating a number of systems, viz., $\text{KClO}_4\text{-RaSO}_4$; $\text{KClO}_4\text{-Pb(RaD)SO}_4$; $\text{KMnO}_4\text{-RaSO}_4$, and others.

For ^{the third group of substances, so-called} anomalous mixed crystals too the lower miscibility limit has been stated in several different instances, viz., systems $\text{NH}_4\text{Cl-FeCl}_3\text{-H}_2\text{O}$; $\text{NH}_4\text{Cl-MnCl}_2\text{-H}_2\text{O}$; $\text{Ba}(\text{NO}_3)_2\text{-methylene blue}$; and others. It has been found that with certain microcomponent concentrations a true stable equilibrium between these crystals and the solution is possible, in accordance with Khlopin's law ⁽⁵⁾.

Khlopin's investigations have shown that in the case of isomorphous substitutions crystals become homogeneous through a long recrystallization of the precipitate in the saturated solution and also when the crystals of macrocomponent are precipitated from a supersaturated solution by rapid mechanical stirring.

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It is well to note that the latter technique (the isothermal breakdown of supersaturation) led in several experiments of different authors to an non-homogeneous distribution of the microcomponent in crystal layers, obeying Doerner-Hoskins's logarithmic law ⁽⁶⁾:

$$\ln \frac{a}{a-x} : \ln \frac{b}{b-y} = \lambda$$

where a and b are the amounts of macro- and micro-component in solution before the ^{precipitation} [liberation] of the solid phase; (a-x) and (b-y) are the respective amounts after ^{precipitation} [liberation]; λ is the fractionation coefficient.

The work done by Khlopin and collaborators was of great value in principle, but the mechanism underlying the formation of anomalous mixed crystals was not brought to light and the application of the distribution law to systems containing crystals of mosaic structure was rather formal. The nature of the internal adsorption systems described by Hahn ⁽⁷⁾ was not explained either.

Soviet radiochemists have done much to develop research on the line initiated by Khlopin. In recent years they have secured abundant experimental evidence in support of his conclusions. From these data it is evident at the same time that in the case of anomalous mixed crystals and internal adsorption systems cocrystallization phenomena are a matter of great complexity.

Grebenschikova and collaborators ⁽⁸⁾ have shown that on isothermal breakdown of supersaturation in

solutions the distribution of the microcomponent can follow both Khlopin's linear law and the logarithmic formula of Dörner-Hoskins. Under constant conditions of experiments the behaviour of the microcomponent depends on the solubility of the precipitate, on its ability to give supersaturated solutions, on the relative rate of crystal growth and on other factors. To put system K_2SO_4 - $Ce_2(SO_4)_3$ - HNO_3 - H_2O as an example, a very good coincidence with Khlopin's law was observed ($D = \text{const}$) when HNO_3 was a 1.5 N solution, whereas with an 0.5 N solution of HNO_3 Dörner-Hoskins's law was followed ($\lambda = \text{const}$). The solubility of the double salt precipitate is considerably higher in 1.5 N HNO_3 than in 0.5 N HNO_3 , which makes its recrystallization easier.

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In studying the coprecipitation of Am^{3+} , La^{3+} and Ce^{3+} with K_2SO_4 it was found that anomalous mixed crystals having no lower solubility limit are formed in the K_2SO_4 - $La_2(SO_4)_3$ -0.5 N HNO_3 , K_2SO_4 - $Ce_2(SO_4)_3$ -0.5 N HNO_3 and K_2SO_4 - $Am_2(SO_4)_3$ -0.5 N HNO_3 systems. La^{3+} , Ce^{3+} and Am^{3+} are distributed within the K_2SO_4 crystals according to a logarithmic law with constant λ values, which are distinct for each of the microcomponents, viz., $\lambda_{Ce} = 15$, $\lambda_{La} = 17$ and $\lambda_{Am} = 42$. These values of λ do not change when the respective elements are present together. Foreign ions (Fe^{3+} , Al^{3+} , Bi^{3+}) have no effect on the value of the fractionation coefficients found, and so the formation of internal adsorption systems is here impossible.

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For systems with a lanthanum salt, $La_2(C_2O_4)_3 \cdot 9H_2O$ or $K_3La(SO_4)_3$, as a macrocomponent and with Y^{3+} , Eu^{3+} ,

and the lower miscibility limit was absent. Especially interesting is the fact that tetravalent plutonium enters into the lattice of lanthanum salts to form in spite of the difference in valence, ordinary mixed crystals instead of anomalous. Its concentration varied from 2×10^{-3} to $7. \times 10^{-7}$ M in the case of the double potassium lanthanum sulphate as macrocomponent and from 4×10^{-6} to 5×10^{-9} M in the case of lanthanum oxalate.

Essential also is that all of the multivalent ions investigated (trivalent - Y^{91} , La^{140} , Ce^{141} , Am^{241} ; tetravalent - Zr^{95} and Pu^{239}) are captured by the K_2SO_4 crystal lattice without a lower miscibility limit. It has been suggested by the cited authors that the microcomponents mentioned enter into potassium sulphate lattice in the form of double salts, which are formed at the surface of K_2SO_4 . Also the penetration of Pu^{4+} into the $\text{K}_3\text{La}(\text{SO}_4)_3$ lattice is explained by the formation of a complex ion $[\text{Pu}(\text{SO}_4)_3]^{2-}$ in the sulphate solution, this ion being able to replace the $[\text{La}(\text{SO}_4)_3]^{3-}$ ions whereby an anion is introduced into the interstitial space to compensate the charge. [Increase or decrease in the K_2SO_4 concentration in solution brings about a reduction of the fractionation coefficient of the $[\text{Pu}(\text{SO}_4)_3]^{2-}$ ion. Similar results of these investigations it has been proposed that the instability constants, K_{inst} , of complex ions formed by the microcomponent should be computed from the observed values of the fractionation

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coefficients. Thus, for the oxalate complex $\text{Pu}^{4+} - / \text{Pu}(\text{C}_2\text{O}_4)/^{2+}$ the following formula was used:

$$K_{\text{in.}} = \frac{[\text{C}_2\text{O}_4^{2-}]}{\left[\frac{D_f}{D_0} - 1 \right]}$$

Here D_f is the fractionation coefficient in the presence of complex formation; D_0 is the fractionation coefficient when no complex is formed. The value of $K_{\text{in.}}$ was found to be $5.2 \times 10^{-7} \pm 10\%$.

investigating the anomalous mixed crystals
 Mrs E.M. Ioffe (9) has arrived at a similar conclusion. According to her, the formation of anomalous mixed crystals, in some cases at least, is due to the structural analogy between the macrocomponent and the complex salts formed by it with the microcomponent rather than to the crystallographic similarity of the initial substances, as observed in the case of a true isomorphism.

She experimented with systems consisting of NH_4Cl and of chlorides Fe^{3+} , Mn^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} , and Co^{2+} , and with some organic systems containing inorganic elements. Of the nine systems she investigated six undoubtedly had a lower limit for the formation of mixed crystals (D was observed to decrease sharply with ^{decreasing} the microcomponent concentration in solution). For the $\text{NH}_4\text{Cl} - \text{CuCl}_2$ and $\text{NH}_4\text{Cl} - \text{MnCl}_2$ systems the fractionation coefficient remains invariable within a wide range of concentration. In this case the complex ion $[\text{MnCl}_4 \cdot 2\text{H}_2\text{O}]^{2-}$ seems to replace the $2 \text{NH}_4^+ \cdot 4\text{Cl}^-$ groups in the NH_4Cl lattice.

In the systems containing iron or chromium chlorides the complex ions $[\text{FeCl}_5 \cdot \text{H}_2\text{O}]^{2-}$ and $[\text{CrCl}_5 \cdot \text{H}_2\text{O}]^{2-}$ are present, which are incapable of the substitution just mentioned.

Similar results have been obtained with systems containing two microcomponents each, viz., with $\text{NH}_4\text{Cl}-\text{MnCl}_2-\text{CuCl}_2-\text{H}_2\text{O}$ and $\text{NH}_4\text{Cl}-\text{FeCl}_3-\text{CrCl}_3-\text{H}_2\text{O}$. Here manganese and copper retain the values of their distribution coefficients. The distribution coefficient of chromium is somewhat higher in the presence of iron. The reason for this, as suggested by that author, is that on the precipitation of crystals the complex anion $[\text{CrCl}_5 \cdot \text{H}_2\text{O}]^{2-}$ is deposited on the ready portions of the lattice which are formed by the complex anion $[\text{FeCl}_5 \cdot \text{H}_2\text{O}]^{2-}$ isomorphous with them.

M.S.Merkulova and collaborators have investigated the coprecipitation of divalent metal ions with salts forming crystals of sodium chloride structure. The systems studied were $\text{NH}_4\text{I}-\text{PbI}_2$, $\text{NaCl}-\text{PbCl}_2$, $\text{NaCl}-\text{SrCl}_2$ and $\text{NaCl}-\text{CdCl}_2$. It has been found that the microcomponents are slow to come to equilibrium in these systems. This corresponds to the mechanism of solid solution formation. The distribution of the Pb^{2+} , Sr^{2+} and Cd^{2+} ions in the volume of solid phase is uniform, as shown by the fact that fractionation coefficient D is constant for a given concentration of the distributed substance. On the strength of the experimental data obtained it is suggested that formed by microscopic quantities of PbCl_2 , SrCl_2 and CdCl_2 with

NaCl crystals are solid solutions of limited miscibility (¹⁰).

The results obtained in experimenting upon the joint coprecipitation of microscopic quantities of both Pb and Bi with NaCl were used for a quantitative separation of lead and bismuth isotopes. Those experiments had shown that microquantities of PbCl_2 and BiCl_3 were distributed between the crystals and the saturated solution of sodium chloride independently of each other, either having its own distribution coefficient. The absolute values of fractionation coefficient are strikingly different: $D_{\text{Pb}} = 200$, $D_{\text{Bi}} = 0.5$. By a twofold precipitation of sodium chloride from a super saturated solution containing RaD and RaE the lead and bismuth isotopes can be separated completely (¹¹). The same authors used non-isomorphous systems $\text{NaCl-PbCl}_2\text{-H}_2\text{O}$ and $\text{NaCl-CdCl}_2\text{-H}_2\text{O}$ for a thorough study of the mechanism underlying the formation of limited solid solutions. To that purpose they investigated the dependence of the microcomponent concentration in the solid phase upon the overall concentration of the impurity in the system. An upper miscibility limit was observed in these systems, and a Langmuir type of equation (¹²) was found to describe the variation of the impurity concentration in the solid phase as a function of its overall concentration in the system.

Mechanism of precipitation
 Subjected to a theoretical discussion *mechanism of the* [was] the formation of solid substitution solutions at the main crystallization stages, viz., when the crystallization centres (nuclei) are forming and during crystal growth. These theoretical considerations were checked by experiment. To reveal the coprecipitation regularities during nucleation of the crystals the fluctuation theory was resorted to. It has been shown

that no equilibrium is established when the radioelement is being distributed between the nuclei and the supersaturated solution in which they are forming. The concentration of the radioelement in the volume of the nuclei is close to its concentration in the initial solution. On the modern crystallization concepts it has been established that the impurity can be so distributed as to be either in or out of equilibrium depending on the conditions of crystallization: the solubility, surface energy and density of the macrocomponent crystals, the mode and rate of nucleation, the temperature, etc. By adjusting suitably these factors the recrystallization of the solid phase can be repeated many times during an experiment, and the distribution coefficient D in equilibrium can easily be determined. On the other hand, the conditions of crystallization can be so chosen that there will be no recrystallization during the experiment. In the latter case the regularities in the coprecipitation of microimpurity with the growing macrocomponent crystals can be studied (¹³).

Investigated by experiment was the formation of the solid macrocomponent phase on the precipitation of NaCl crystals from a slightly supersaturated solution when it is being stirred. It has been found in these experiments that accumulation of the radioelement in the precipitate takes place when a constant number of nuclei of critical size are in progress of growth. In studying the phenomena taking place at the surface of a growing submicron a quasi-crystalline model of liquid was used. The radioelement coprecipitation mechanism was considered at a stage

of dynamic adsorption exchange between the crystal surface and the solution and at a stage, when a new monomolecular layer is being regularly deposited on the surface of the crystals of carrier. The main relations were deduced which govern the transition of the impurity to the surface layer and the distribution of the radioelement in the volume of the carrier crystals under different conditions of crystallization. The theoretical regularities were borne out by experiments with several different systems, viz., NaCl-PbCl_2 , NaCl-CdCl_2 , NaCl-TlCl and NaCl-InCl_3 ⁽¹⁴⁾.

Theoretical investigations on the distribution of ions between the solid and liquid phases and on the kinetics of the process by which the respective equilibria are attained have been made by Kirgintsev ⁽¹⁵⁾. His thermodynamic calculations have revealed a profound analogy between the coocrystallization and adsorption phenomena. He obtained for the coprecipitation isotherm the equation

$$K_X^m = b(Z_1 - \Gamma),$$

where K_X is the distribution coefficient (the ratio of the microcomponent concentration in the solid phase to its concentration in the liquid phase); m is the number of ions into which the microcomponent $A_{n_1} B_{n_2}$ dissociates ($m = n_1 + n_2$); $b = (K_1 \cdot K_1' / K_2 \cdot K_2')$ (K_1' and K_2' are the rate constants of adsorption, respectively desorption, of the microelement at the crystal surface; K_1 and K_2 are the rate constants of the "molecules" leaving the surface for the volume of the crystal and of those coming to the surface from within respectively); Z_1 is the amount of microcomponent in a unit volume of the crystal when the concen-

tration of the microcomponent in the solution is infinitely large, whereas the macrocomponent concentration is invariable Γ is the microcomponent content in one mole of the crystal.

In the region of poor filling

$$K_x^m = b(d' c_0 - \Gamma)$$

where d' is a constant, c_0 is the microcomponent concentration in the initial solution.

This equation accounts for the appearance of a lower miscibility limit: as the microcomponent concentration goes down so does also the value of the distribution constant, i.e., the mixed crystals become lower in the microcomponent. The absence of a lower miscibility limit is connected with the formation of homogeneous anomalous mixed crystals, which from the thermodynamical standpoint represent a single phase.

The kinetic method was used in computing the distribution of cations between the solid and liquid phases for anomalous mixed crystals when no microcomponent aggregates are formed in the macrocomponent crystal. Equations establishing a relation between the time of recrystallization and the amount of microcomponent in the precipitate were obtained. These equations for true isomorphous systems remind of a simple exponential law of exchange, differing only in pre-exponential factors.

Marin and Pliner ⁽¹⁶⁾ too have investigated the formation mechanism for anomalous mixed crystals and theoretically derived analytical expressions for the activity of the microcomponent in heterogeneous systems. There are grounds to suggest that no anomalous mixed crystals will form unless the number of microcomponent particles in 1 millilitre of

solution, C , exceeds a certain critical value, $C_{cr.}$, at which the monolayer on the crystal surface becomes unstable and disintegrates into two stable surface phases. If $C > C_{cr.}$, the monolayer of microcomponent (the "guest") is stable enough to defy its replacement by the macrocomponent (the "host") when the latter is in progress of crystal growth. If $C < C_{cr.}$, no formation of condensed phase will take place.

Considered is also the role in those processes of the association of particles on cocrystallization to form complexes in the broad sense of the word.

Gorstein (¹⁷) has published a series of papers on the role of the physico-chemical state of the impurities in the processes of their fractionation on crystallization or when inorganic substances are deposited from aqueous solutions.

New data have been obtained on the distribution of the microcomponent between the melt and the crystal phase. V.R.Klokman and collaborators (¹⁸) have found that anomalous mixed crystals do form in the LaF_3 - RaF_2 system when lanthanum fluoride is ^{precipitated} (liberated) from the KF or RbF melts, yet there is no lower limit of miscibility. The value of the fractionation coefficient depends on the chemical nature of the second component: the value of D is about 2.5 times as great in the RbF melt as in the KF medium. It is of interest to note that enriched by the microcomponent in these experiments was the solid phase and not the melt, as is observed usually. The introduction of microimpurities (Ca^{2+} , Ba^{2+}) had no influence on the value of the fractionation coefficient. Emphasized in this work, as, indeed, in

some other investigations, is the important role of complex formation in the melt in course of fractionation.

The study of the distribution of RbCl_2 labelled with ThB between the melt and the LiCl , NaCl , KCl and KBr crystals has shown that the halides of alkali elements having the lattice of NaCl type do not capture lead in appreciable quantities. So there is a striking difference between the behaviour of lead ions in a melt and in aqueous solutions. The authors of the papers cited explain it by a strong dependence of the fractionation coefficient upon the temperature.

Adsorption of radioactive isotopes from solutions has been the object of a number of investigations. Thus I.E. Starik and collaborators (¹⁹) have been engaged on the study of some essential problems bearing on the relation of adsorption processes to such factors as the chemical properties of the ions, the nature of the sorbent and the environmental conditions. Heavy elements of the main subgroups in I and II groups of the periodical table are adsorbed on glasse and other sorbents of ionite type in the form of positively charged ions, being unable to form colloids even in ultra-small concentrations. Heavy elements in the III - VIII groups form true colloids, starting from $\text{pH} = 2-7$ upwards. The adsorption of these elements is based on their hydrolytic capacity. On the adsorption curve there is always a maximum. The rise of the curve is due to the ionic portion, its decline, to the colloidal portion.

I [The adsorption of negative ions has been studied

on phosphates. The highest adsorptive capacity towards the HPO_4^{2-} ion was displayed by glasses which had the highest dielectric constant and whose surface was the least negatively charged. The presence on the glass surface of foreign multivalent cations increased the sorptive capacity.

Adsorption of radioactive isotopes Zr^{95} , Nb^{95} , Th^{234} , Pa^{233} , Tl^{204} and Cs^{137} without ion exchange was measured on paraffine and fluoroplast-4 (²⁰). In a nitric acid solution (0.1 - 5 N HNO_3) a notable adsorption of Zr^{95} , Nb^{95} , Th^{234} and Pa^{233} is observed, owing, probably, to the formation in the aqueous phase of neutral complexes corresponding to the general formula $[\text{Me}(\text{OH})_x(\text{NO}_3)_y]^0$. If NH_4NO_3 and KNO_3 are added, the adsorption diminishes several times, apparently on account of salting out effect. If the acidity of the solution increases to 12 N, the adsorption of Zr^{95} and Th^{234} decreases, whereas the adsorption of Nb^{95} and Pa^{233} changes insignificantly. The author's explanation of this fact is that Zr^{95} and Th^{234} form a complex with HNO_3 . The Cs^{137} and Tl^{204} ions (in monovalent form) are not adsorbed either on paraffine or on fluoroplast-4, because they refuse to form neutral compounds under the investigated conditions.

The regularities displayed by the adsorption of radioisotopes on various precipitates have been investigated by N.E. Brezhneva and collaborators (²¹). Especially, when the secondary adsorption of cations on an iron oxyacetate precipitate was measured quantitatively with allowance for complex formation, and the pH value of the solution as well as the surface area of the precipitate formed were determined

5 it was found that within a wide range of concentration of the adsorbed cations the adsorption isotherm is described by

$$q = Ae^{1/n},$$

where q is the amount of the substance adsorbed in 1 g of precipitate. The coefficient n is independent on the pH of the solution and is a function of the charge of the adsorbed cation, whereas the coefficient A depends on the pH value, which influences the specific surface area and the formation of an electric double layer at the solid body - solution interface.

It has been established that the adsorption isotherm for cations on precipitates of the hydroxide type can be represented in a developed form by equation

$$q = \frac{E}{E_0} A_0 (pH - pH_0) \cdot 1/n$$

where E/E_0 is a quantity proportional to the specific surface area of the precipitate; pH_0 is a value of pH at which the adsorption of the particular cation begins.

The sorption of various radioactive isotopes (Cs^{137} , $Sr^{89,90}$, Ce^{144} and Ru^{106}) on aluminium hydroxide precipitates has been investigated by S.A.Voznesensky and collaborators (²²). The tests were run at 20° with micro-concentrations of the isotopes. Practically there was no sorption of cesium under test conditions; for the other isotopes sorption was a maximum at certain pH values, viz., at 7.0 for Ru, at 7.5 for Ce, at 9.0 for Sr. As the temperature goes up, the adsorption of Ce and Ru grows, whereas the adsorption of Sr remains practically invariable. The authors suppose that the Ru and Ce ions are adsorbed by a ion exchange

mechanism, while the sorption of strontium is due the formation of aluminate.

Considerable work has been done on the chromatography of radioactive elements. General questions concerning the use of ionites in radiochemistry have been dealt with by B.P.Nikolsky (23). If the salt background (the concentration or activity of the macrocomponent) is constant, the activity coefficient of the microcomponent will be constant too. The coefficient of microcomponent ion distribution between the ionite and the solution (α_1) is independent on the microcomponent concentration:

$$\alpha_1 = \frac{\Gamma_1}{C_1} = K^{z_1} \left(\frac{\Gamma_2}{C_2} \right)^{z_1/z_2} f(\gamma) = \text{const}$$

Here C_1 and C_2 are the concentrations of the respective ions; $f(\gamma)$ is a factor containing the activity coefficients of the ions in the resin and in the solution; Γ_1 and Γ_2 are the amounts of adsorbed ions belonging to the microcomponent and macrocomponent respectively; z_1 and z_2 are the valencies of the respective ions; K is the exchange constant.

This equation is generally used in solving various radiochemical problems.

Some theoretical problems connected with the use of the frontal method in the chromatography of ion exchange complex formation for the production of pure preparations of radioactive isotopes have been tackled by K.V.Chmutov and co-workers (24). The authors have analyzed the principal factors controlling zonal motion in a frontal analysis of a mixture of complex ions present in macro- and microconcentrations. By means of the equations they have obtained for adsorption isotherms and for the frontal motion of the second component,

the coefficient of microcomponent enrichment and that of purification of the macrocomponent can be calculated.

This method has been tried by experiment on a mixture of ethylenediaminetetraacetate complexes of Ca^{2+} (macrocomponent) and Sr^{2+} (microcomponent). The results are in good agreement with the theory. With regard to the purification of the macrocomponent, the frontal method has been found to be 18 times as efficient as the ion-exchange displacement method.

[The influence of temperature on ion-exchange equilibrium has been studied by Matorina and Popov (²⁵). Their theoretical statements are confirmed by an experimental analysis of temperature variations in ion-exchange sorption of Ca^{45} and of fragmentary isotopes - Cs^{137} , Sr^{89} and Ce^{144} - Pr^{144} .

An important cycle of research is formed by investigations into the action of radiation on ion-exchange resins. Various types of resins in different media have been investigated. They were acted upon by X-rays, gamma-rays and by high energy electrons. Proskurnin and co-workers (²⁶) have shown that the radiation destruction of ionites is accompanied by increase in their static exchange capacity. This is evidence that the number of ion-exchanging functional groups, especially hydroxyls, increase in the ionites.

[Senyavin et al. (²⁷) have investigated three typical ionites for their resistance to X-rays and gamma-rays, viz., KM-1 (sulphocationite of the phenol-formaldehyde type), KM-2 (sulphurated copolymer of styrene and divinylbenzene), and

~~KY~~^h-4 (saponification product of a copolymer formed by methyl metacrylate and divinylbenzene with carboxyl functional groups). It has been found that the effect of radiation is to induce competing processes of destruction and cross-linking. The chemical alterations caused by radiation are deeper in resins of aliphatic structure than in those aromatic character. Qualitatively the functional groups of the cationites studied are resistant to radiation, though they decrease somewhat in quantity. The highest resistance was shown by the ~~KY~~^h-2 cationite.

Kiseleva and Chmutov (²⁸) have subjected the KY-2 cationite to bombardment by high energy electrons. As the radiation dose increased from 10^{21} to 10^{24} eV per g of resin the exchange capacity for the functional group HSO_3^- diminished, and new ion-exchange groups with $\text{pK} = 4.3$ and 7 made their appearance. The resin partly passed to a soluble state. By irradiating the KY-2 cationite in different solutions (0.5 N HNO_3 , 0.5 N CH_3COOH and 0.25 N solution of ammonium lactate) new functional groups can be made to appear even with a dose of 10^{22} eV per g of resin.

Work in the field of chromatographic separation of radioactive isotopes has been so extensive that only a few instances can be referred to here. Especially strong is the number of investigations concerned with the separation of fragmentary rare earth isotopes. Tunitsky and collaborators (²⁹) have developed a theory of chromatographic separation of rare earth elements in which account is taken of statistical factors (the ratio of sorption coefficients

of the separated ions) and of kinetic factors (the rate of diffusion of the ions in the sorbent grains), their rate of diffusion to and from the grains in a flow of solution, longitudinal mixing and diffusion). Experiments have shown that the diffusion coefficients of rare earth elements grow in the order of their atomic numbers. On the suggested theory the optimal conditions for the separation process and its duration can be computed.

The separation of fragmentary rare earth elements by means of lactic acid and pyrophosphoric acid solutions has been studied by Maslova, Nazarov and Chmutov (³⁰). The authors measured the stability constants of lactate complexes of some rare earth elements and were able to show that the use of pyrophosphoric acid for the chromatographic separation of rare earth elements holds promise of success.

Preobrazhensky et al. (³¹) determined the separation coefficients for all rare earth elements, when ammonium lactate is the complex former, and compared them with the available literary data on the oxyisobutyrate and glycolate of ammonium. The authors found that heavy rare earth elements are separated better with ammonium lactate, while for those of smaller atomic weight ammonium oxyisobutyrate is preferable.

To find out how the processes involved in the chromatographic separation of Y from Ce and of Pm from Nd are influenced by the number of carbon atoms in the chain of same α -oxyacids has been the object of experiments arranged by Spitsyn and Voitekh (³²). They made use of the following acids as complex formers: glycolic, lactic, α -oxyiso-

butyric, α -oxyisovaleric and α -oxyisocaproic. The experiments were run by a static method as well as dynamic. It has been found that the separation coefficient of rare earth elements is higher the stronger the proton bond in the α -oxyacid, i.e., the weaker the acid. Increase in the size of the addend (e.g., in the case of α -oxyisocaproic acid) brings about a weakening of the complex. Therefore α -oxyisobutyric acid is the best eluant.

Lavrukhina and co-workers (³³) have suggested the use of trioxylglutaric acid for the separation of fragmentary rare earth elements (La, Ce, Pr, Nd). She has also studied the effect which the quantity of elements has on the shape and position of the peaks on the yield ~~curve~~ curve in chromatographic ion-exchange separation of rare earth elements. As the quantity of elements goes down the rate of their washing out goes up in a number of cases. This is probably because the equilibrium in the washing out solution is shifted towards the complex form. With ultrasmall concentrations the observed shift of the peaks can unfavourably affect the outcome of the separation process.

For some closely related elements the chromatographic methods of their separation have been made more efficient by B.N. Laskorin and collaborators (³⁵). This they achieved by the use of appropriate complex formers, where by diminishing the effective concentration of the ions separated, which in first approximation is tantamount to decrease in the quantity of the separated elements. Difference in the constants of complex formation is prone to increase the separation coefficient. The authors have investigated nine specimens of cationites and 12 complex formers for

the separation of radium and barium. Most effective were the following acids: citric, nitrilotriacetic and ethylenediaminetetraacetic. The rate of production for barium was 50 kg/hour per 1 m² of column cross-section.

Spitsyn and Kuzina (³⁶) liberated a few milligrams of technetium from impurities by a chromatographic technique. Spitsyn and D'yachkova (³⁷) evolved a chromatographic method for the separation of protactinium, zirconium, titanium and niobium in a column with manganese dioxide. The sorption of Pa and Nb from 10 N HNO₃ permits Zr and Ti to be separated. Conditions for the separate washing out of Pb and Nb from the column were chosen after studying the coefficient of their distribution between MnO₂ and the NH₄F solutions. By this method weighing ^{ponderable} quantities of radiochemically pure Pa²³¹ were obtained.

Inorganic ionites are of great interest on account of their resistance to radiation. Kraus (³⁸) is known to use zirconyl phosphate to this purpose. In the Soviet Union zirconium based ionites have been investigated by Bresler and co-workers (³⁹), viz., the sulphide, chromate, arsenate, oxalate and carbonate of zirconyl. The investigations have shown that all of these compounds have ion exchange properties. When taken in the H⁺ form, they secure a good separation of related elements, e.g., Ca²⁺-Mg²⁺, Sr²⁺-Ca²⁺, and others. As the washing ^{out} solution, 0.05-0.5 N HCl was employed. The enrichment obtained for ^{the} microcomponent ranged from 0.5 x 10² to 10⁴.

Soviet radiochemists have been paying considerable attention to problems connected with the separation of radioactive elements by extraction. As is well known, the extra-

have found world-wide application in radio-chemical industry for the separation of uranium, plutonium and fragmentary elements, as well as for the production of pure uranium compounds. Experience accumulated in this field was extended to other radioelements, where it contributed to considerable progress. And though applied radiochemistry is beyond the scope of this review it seems appropriate to dwell briefly on the work done in the USSR in connection with the main extraction techniques.

Vdovenko and collaborators (⁴⁰) have investigated the solubility of various hydrates of uranyl nitrate in diethyl ether and used the methods of physico-chemical analysis for determining the composition of the compounds here formed and containing water and bound solvent at a time. A systematic study has also been carried out of the uranyl nitrate distribution between aqueous solution and diethyl ether.

Vdovenko and Smirnova (⁴¹) have measured the distribution of uranyl nitrate between aqueous solutions and various ethers and esters. The highest equilibrium constants of the processes taking place here were found with diisobutyl ether, chloroform, isobutylbenzoate and dibutyl ether. Moreover the authors investigated the composition uranyl nitrate hydrates formed by extraction of aqueous solutions with diethyl ether and dibutyl ether in the presence of salting out agents (KNO_3 , NaNO_3 , $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$). In diethyl ether the salts capable of binding water decrease the hydration of uranyl nitrate. This does not occur in dibutyl ether, apparently because the hydration of uranyl nitrate in this solvent is slight. Addition of diluents

... brings about a decrease in the hydration of uranyl nitrate and the extracting power of the solvent is reduced too.

Problems connected with the structure of the coordination sphere of uranium in various organic solvents have been discussed by Vdovenko et al. (⁴²).

Shevchenko and co-workers (⁴³) have investigated the use of tributylphosphate (TBP) as a solvent. They measured the polarization and dielectric constant of TBP mixtures with various diluents and came to suggest that the distribution coefficients of uranyl nitrate are definitely connected with the polar properties of the TBP-solvent system.

Investigation of the influence of TBP hydrolysis products on the extraction of plutonium has shown that practically this process is not affected if the admixture of monobutyl phosphate is below 0.001 mol/l or that of dibutyl phosphate is below 0.0001 mol/l. Yet with higher quantities of these substances the distribution coefficient of plutonium rises considerably, owing presumably (⁴⁴) to complex formation in the aqueous phase.

Rosen and Moiseenko (⁴⁵) have investigated the influence which the concentration of HNO_3 and uranyl nitrate exert on the distribution of Pu (IV) and Pu (VI) in the case of extraction with a 20 % solution of TBP in Hydrogenated kerosene. In the absence of uranium the increase of HNO_3 concentration leads first to increase and then to decrease of the Pu distribution coefficients. The dependence of plutonium distribution coefficients upon the acidity in the presence of uranium was found to be different for Pu(IV) and Pu (VI). The observed relations can be accounted

for by the fact that the salting out effect of macronitrates in the aqueous phase is combined with the displacing effect in the organic phase.

[Experiments with the extraction of uranium by TBP from hydrochloric acid solutions have shown that the compound $\text{UO}_2\text{Cl}_2 \cdot 2\text{TBP}$ is formed in the organic phase (46,47).

A large number of different solvents have been tried for the extraction of uranium, plutonium and other radioactive elements.

Laskorin, Zefirov and Skorovarov (48) have investigated some dozens of organic solvents which seemed well fitted for the extraction of uranium from solutions and ore pulps. Among them were esters of carboxylic acids, phosphoric ester, phosphinic ester as well as liquid cationites and anionites. Some of these substances were used with diluents. Most promising for uranium extraction from nitrate media are isomyl acetate, dimethyl phthalate, dibutyl ether and a 5-10% solution of TBP in kerosene.

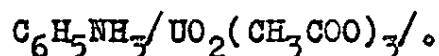
For uranium the diisomyl ether of methylphosphinic acid proved to be effective as a solvent. With it the distribution coefficients are higher than with TBP. The composition of the complexes which this extracting agent forms with uranyl nitrate and HNO_3 has been determined (49).

A systematic investigation of the complex formation by uranyl nitrate with various organo-phosphorus compounds has been carried out by M.F. Pushlenkov et al. (50).

[The authors have found the phosphoryl group to play an important part in the formation of uranium complexes:

the complex formation constants increase in the series of addends $(C_4H_9O)_3PO \longrightarrow (C_4H_9)_3PO$. The stability constants of complex compounds formed by uranyl with TBP, di-n-butyl ether, n-butyl-phosphinic acid and tri-n.-butyl-phosphine oxide have been determined.

It has been shown that an acetate compound of uranium can be extracted with aniline (⁵¹). Thereby a triacetate complex is formed with aniline in the external sphere:



The application of the extraction technique to processes of separation and purification of various radioelements has been tried by many workers.

Shevchenko and collaborators (⁵²) have described the extraction of protactinium with alkylphosphoric acids. The experiments were run with Pa^{233} in nitrate solutions. The highest distribution coefficients were displayed by dibutyl phosphate, diisobutyl phosphate and diisoamyl phosphate. Used as diluents were isoamyl acetate, dibutyl ether, hydrogenated kerosene and some other products which did not affect the extraction yield. The protactinium distribution coefficients varied proportional to the square of the extracting agent concentration in the organic phase.

The extraction of protactinium with mono- and di-isoamylphosphoric acid has been studied by those authors in greater detail. They suggest that the extracting agent here forms complexes in the aqueous phase. Going over into the organic phase is, apparently, the compound PaK_5 (K being the radical of isoamyl-phosphoric acid), while the products of its partial hydrolysis, $/Pa(OH)_3K_3/^-$, $/Pa(OH)_4K_2/^-$ and

The extraction of pentavalent neptunium has been described by Alimarin and co-workers (⁵³). [The tests were run with indicator quantities of Np^{239} and ponderable quantities of Np^{237} .] A solution of 1-nitroso-2-naphthol in n-butyl alcohol and in isoamyl alcohol with pH 9-10 was the extracting agent. Up to pH 6 no extraction of neptunium will occur. Forming in the extraction process seems to be a compound of the NpO_2^+ ion with 1-nitroso-2-naphthol. This technique can be used for the separation of neptunium from plutonium and uranium (for their extraction in the presence of 1-nitroso-2-naphthol the solutions should be adjusted at pH 1.0-1.5 and 3.5-4.0 respectively).

Extraction with methylethyl ketone was used for the separation of technecium from irradiated molybdenum (⁵⁴). For salting out KOH, K_2CO_3 and $(\text{NH}_4)_2\text{CO}_3$ were employed. Molybdate solutions too are endowed with salting out effect. The re-extraction of technecium from the organic phase was done with a 6 N solution of K_2CO_3 .

Diamylphosphoric acid was used by Brezhneva and co-workers (⁵⁵) for the separation of rare earth fragmentary elements by extraction. The study of this process has revealed that in the region of low hydrogen ion concentrations an organic salt of rare earth elements is the compound extracted. With high hydrogen ion concentrations the extraction mechanism is different: extracted here are $\text{Me}(\text{NO}_3)_3 \cdot \text{H}_2\text{A}_2$ solvates (H_2A_2 standing for diamylphosphoric acid), formed under participation of the oxygen of the phosphoryl group.

The effect of uranyl nitrate on the distribution of Ca, Ce, Sr and La between the aqueous solution and methylbutylketone has been investigated by Vdovenko et al. (56). The distribution coefficients of these elements increase as the concentration of uranyl nitrate rises, which fact is ascribed by the authors to the formation of $\text{MeUO}_2(\text{NO}_3)_2$ compounds in the organic phase.

Considerable work has been done on the chemistry of individual radioelements. Special attention was given to the study of plutonium and the nearest transplutonium elements.

Some unknown or scarcely studied plutonium compounds were synthesized and their properties described. By evaporating a hydrochloric acid solution of hexavalent plutonium in vacuo a crystalline plutonyl chloride, $\text{PuO}_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ was obtained (57). Plutonyl fluoride, PuO_2F_2 , was produced by the action of liquid hydrogen fluoride on a cooled plutonyl chloride solution. The solubility of this compound in water (1.07 g/l at 25°C), its absorption spectra and crystal structure were determined (58). V.V. Fomin et al. (59) has synthesized plutonium tribromide by the action of gaseous HBr at 500°C upon plutonium oxalate (IV).

The properties of nitric acid solutions of hexavalent plutonium have been investigated (60). The hydrolysis reaction constants of plutonyl ion have been computed, and the hydrate of plutonyl nitrate, $\text{PuO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ has been obtained in the pure form. The radiolytic reduction of Pu(VI) in nitrate solutions under the action of its own radiation was also investigated. It was found to proceed at

the expense of atomic hydrogen formed on the radiolysis of water. Pu (VI) is reduced in the form of hydroxy compounds, e.g., $\text{PuO}_2\text{OH}^\diamond$. First Pu (V) is formed and afterwards Pu (IV), which disproportionates to Pu (VI) and Pu (III).

The conditions of disproportionation of Pu (IV) and Pu (V) in HNO_3 solutions have been studied in detail (⁶¹).

[At the start of the process the disproportionation of Pu (V) proceeds as follows: $\text{Pu (V)} + \text{Pu (V)} \rightleftharpoons \text{Pu (VI)} + \text{Pu (IV)}$. Later on, with the accumulation of Pu (III), predominant becomes the reaction $\text{Pu (V)} + \text{Pu (III)} \rightleftharpoons 2 \text{Pu (IV)}$, which brings about an autocatalytic acceleration of the process.]

Investigated was also the solubility of some scarcely studied plutonium compounds, e.g., plutonyl oxalate, $\text{PuO}_2\text{C}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ (⁶²), the bisubstituted phosphate of plutonium (IV) (⁶³) and others.

The salicylates of tri- and tetravalent plutonium have been described by Zviagintsev and Sudarikov (⁶⁴).

There have been considerable developments in the chemistry of complex compounds of transuranium elements.

4 Gelman and her co-workers have investigated the carbonate, oxalate and ethylenediaminetetracetate complexes of plutonium. [In paper (⁶⁵) ^{She} is] described the production of the carbonate complexes of plutonium (IV): $(\text{NH}_4)_4/\text{Pu}(\text{CO}_3)_4 \cdot \text{H}_2\text{O}$, $(\text{NH}_4)_6/\text{Pu}(\text{CO}_3)_5 \cdot n\text{H}_2\text{O}$ and $(\text{NH}_4)_8/\text{Pu}(\text{CO}_3)_6 \cdot n\text{H}_2\text{O}$. On their decomposition plutonium (IV) oxycarbonate $\text{PuOCO}_3 \cdot 2\text{H}_2\text{O}$ is formed. A complex carbonate of plutonium (VI), $(\text{NH}_4)_4/\text{Pu}(\text{CO}_3)_5$, has been isolated by Drabkina (⁶⁶). It decomposes to form a monocarbonate, PuO_2CO_3 .

Solubility measurements were used by Moskvina and

Gelman (67) for determining the composition and instability constants of complex oxalate ions $/\text{Pu}(\text{C}_2\text{O}_4)/^{2+}$, $/\text{Pu}(\text{C}_2\text{O}_4)_2/^\circ$, $/\text{Pu}(\text{C}_2\text{O}_4)_3/^{2-}$ and $/\text{Pu}(\text{C}_2\text{O}_4)_4/^{3-}$. They have shown that among the different valence states of plutonium the tendency to complex formation declines in the order $\text{Pu}^{4+} > \text{Pu}^{3+} > \text{PuO}_2^{2+} > \text{Pu}^{2+}$. *Mixed carbonate-oxalate complexes of plutonium (IV) are described in [68].*

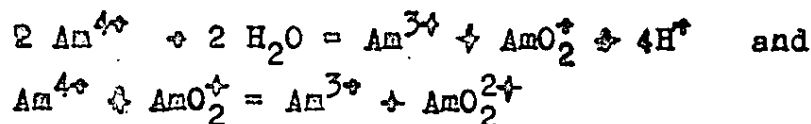
In a pure state some oxalate complexes of plutonium (IV) were obtained by Gelman and Sokhina (69). Unlike the normal oxalate, they are easily soluble. Isolated were the following complexes: $\text{Na}_4/\text{Pu}(\text{C}_2\text{O}_4)_4 \cdot 5\text{H}_2\text{O}$, $\text{K}_4/\text{Pu}(\text{C}_2\text{O}_4)_4 \cdot 4\text{H}_2\text{O}$, $\text{K}_6/\text{Pu}(\text{C}_2\text{O}_4)_5 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_6/\text{Pu}(\text{C}_2\text{O}_4)_5 \cdot n\text{H}_2\text{O}$. They proved stable in aqueous solutions both in the cold and when heated. It is interesting to note that one of these complexes, viz., $(\text{K}, \text{Na})_4/\text{Pu}(\text{C}_2\text{O}_4)_4 \cdot 4\text{H}_2\text{O}$ can exist in two crystal modifications - red and greenish yellow.

Gelman and her co-workers (70) used the ion exchange technique in studying the possibility of a complex formation of pentavalent plutonium with ethylenediaminetetracetic acid (EDTA). Indeed they have established the presence of a complex ion $/\text{PuO}_2\text{Y}/^{3-}$, (Y^{4-} being the anion of EDTA) in the pH 4-5 region. Measurements of the constant of concentration instability of this ion have shown that it is close to the value reported in (71) for a similar complex of neptunium. For ~~complexes~~ trivalent plutonium with EDTA, complexes of the composition PuY^- and PuHY° have been found and their structures discussed (72).

Kondratov and Gelman (72) have investigated oxalate complexes of tetravalent plutonium by means of solubility measurements. The salt $(\text{NH}_4)_4/\text{Pu}(\text{C}_2\text{O}_4)_4 \cdot n\text{H}_2\text{O}$ was isolated by them in the crystalline state. The concentration in-

(7) $/\text{Np}(\text{C}_2\text{O}_4)/^{2+}$, $/\text{Np}(\text{C}_2\text{O}_4)_2/^0$, $/\text{Np}(\text{C}_2\text{O}_4)_3/^{2-}$, $/\text{Np}(\text{C}_2\text{O}_4)_4/^{4-}$ were computed. They were found to have the same order of magnitude as the respective Pu (IV) complexes.

New data have been obtained on the chemistry of americium (⁷⁴). The content of Am (III), Am (V) and Am(VI) in solutions prepared by interaction between AmO_2 and H_2SO_4 has been determined spectrometrically. The results show the existence of two reactions:



Both of them proceed at a high rate, which accounts for the absence of Am (IV) in aqueous solutions.

(7) *mpgsm.*

Moskvin, Khalturin and Gelman (⁷⁵) used a ion exchange technique in studying the formation of complexes by Am (III) with EDTA and with oxalic acid. The structure of the compounds which are formed here, viz., $/\text{Am}(\text{C}_2\text{O}_4)_2/$, $/\text{Am}(\text{HC}_2\text{O}_4)_3/^0$ and $/\text{Am}(\text{HC}_2\text{O}_4)_4/^{-}$, is discussed in their paper.

Progress can also be recorded in the chemistry of fragmentary elements. The object of N.E. Brezhneva and her co-workers (⁷⁶) was to study in detail how the radioisotopes of zirconium, niobium, ruthenium, strontium, barium and rare earth elements are distributed between the precipitate (calcium oxalate, calcium nitrate, iron hydroxide, etc.) and the solution. Developed in these studies was an elaborate scheme for the separation of fragmentary elements. It is based on reactions involving co-precipitation. Thus strontium and

rare earth elements are deposited with calcium oxalate precipitates; zirconium, niobium and ruthenium, with iron hydroxide. Later on the elements are separated by liquid extraction with tributyl phosphate from nitrate solutions. On this scheme strontium-90, zirconium-95, niobium-95, ruthenium-106, promethium-147, cerium-144, europium-155 can be obtained at the laboratory as pure isotopes in quantities varying from 15 millicuries to 15 curies according to their content in the initial solution.

Other radioelements too have been investigated to some extent by Soviet workers. B.P. Nikolsky and collaborators (77) have used an ion exchange technique in studying the formation of complexes by radium and barium in solutions of EDTA and nitryltriacetic acid. At pH 5.5-6.9 radium forms with EDTA a complex of the composition $(RaA)^{2-}$. With nitryltriacetic acid the complex has the composition $(RaX)^{-}$ and is obtained at pH 6-8. The two complex ions are somewhat less stable than the respective barium compounds.

Ziv and Efros (78) measured the solubility of polonium (IV) hydroxide by a microchemical technique, and found it to be $(3.7 \pm 1.5) \cdot 10^{-5}$ mol/l for pH 6.

Capture of protactinium-233 by various precipitates was studied by Nikolaev and collaborators (79). They have found that Pa is precipitated together with almost every poorly soluble compound of Th. However, when thorium fluoride is precipitated, Pa can be held in solution under certain conditions. The authors suggested the method of "similar carriers" ($CaCO_3$ and $CaC_2O_4 \cdot H_2O$) which permits

Pa to be separated quantitatively from the oxycarbonate and oxalate of Th, and transferred to other carriers, such as $\text{Fe}(\text{OH})_3$. A technique for the extraction of Pa with acetone in the presence of salicylic acid has been developed.

Starik and Sheidina (⁸⁰) proposed a convenient procedure for radiochemical purification of protactinium by its precipitation together with zirconium phenyl glycolate.

Spitsyn and Kuzina (⁸¹) have designed a technique for the isolation of technecium from neutron irradiated molybdenum, and investigated the chemical properties of some technecium compounds.

A great many investigations in the Soviet Union have been devoted to the chemistry of uranium and its complex compounds. However the results obtained in this field cannot be reported here on account of the space available.

Considerations of space preclude also a discussion of research connected with the production of radioactive isotopes without carriers, although significant progress has been made in this field too.

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THE DEVELOPMENT OF RADIATION CHEMISTRY

IN THE U.S.S.R.

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Introduction

The study of chemical changes of substances brought about by high energy radiation has begun its rapid development in connection with the availability of the power ionizing radiation sources. The development of radiation chemistry was stimulated first of all by requirements of nuclear engineering and problems of the reliable protection against the hazardous radiation. On the other hand, the radiation chemistry deals with the phenomena called forth by high-excited and of high reactivity particles, i.e. ions, free radicals,

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and molecules. The latter is caused by the fact that energy of ionizing radiation is many times as large as the chemical bond energy. The generation of excited particles mentioned is the main distinctive feature of radiation-chemical processes in comparison with the photochemical those where such phenomena do not almost occur. This circumstance has also promoted to the growth of interest in radiation chemistry and its uses in practice.

Russian and soviet scientists made a substantial contribution in the development of radiation chemistry. Thus, among the first investigators having observed chemical effects of ionizing radiation upon diverse compounds there was N.A.Orlov. In 1904-1906 he founded ¹ that paraffin, wax, stearic acid and other solid organic substances converted into liquid resinous products. In 1910 N.D.Zelinsky ² placed in a sealed tube some little crystals of radium bromide containing 0.5 mg of pure radium and 1.5 ml of cyclohexene (C_6H_{10}). The investigation carried out after several years revealed the deposition of free carbon on surface of the bromide crystals, the liquid decomposition products being consisted not only of hydrocarbons more simple than cyclohexene but, also, of more heavy hydrocarbons synthesized under action of alpha particles emitted by radium. As an intermediate process, apparently, dehydrogenation of the original material occurred.

N.D.Zelinsky stated that relative processes could take place in the nature under effects of radiation of radium contained in rocks.

[Modern] development of radiation chemistry in this country has begun in the post-war years, being caused by uses of nuclear power for various purposes. This period is characterized by rapid development of wide-scale research work embracing more and more diverse classes of compounds and reaction types and, on the other hand, by employment of modern research techniques involving gas-liquid chromatography, electron paramagnetic resonance, mass spectrometry and so on for identification of radiolysis products and for elucidation of the reaction mechanism. As ionizing radiation sources nuclear reactors, spent heat releasing elements of atomic power reactors, γ -ray sources of Co^{60} and Cs^{137} , α -emitters such as radon and polonium preperates, betatrons (including these with extracted electron beams), electron accelerators permitting both continuous and pulsed irradiation, X-ray installations and so on are employed.

These are radiation-chemical research laboratories in various regions of the USSR. A number of the Moscow research institutes are carrying out investigations in this field. Radiation-chemical investigations are accomplished in the Ukrainian SSR, Georgian SSR, Uzbeck SSR and other republics having atomic reactors. The fact that in recent three years about three hundred publications on this topic have been issued by soviet investigators illustrates the development of the radiation chemistry in this country. In 1957 the first All-Union conference on the radiation chemistry was held in Moscow, where 56 papers were reported and discussed ³.

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A large number of the soviet investigations in this field was reported on the other scientific congresses and conferences in this country as well as abroad ⁴⁻¹⁰.

[Authors of this paper] shall, in the main, describe the most important directions of research in the radiation chemistry in the USSR and also shall review some interesting papers published in 1958-1960. [The previous soviet works are published in form of separate collections ¹¹⁻¹², transactions of a number of conferences ⁴⁻⁷, and are also told in reviews ¹³⁻¹⁶ and booklets ¹⁷⁻¹⁸ edited in the USSR.

2. Radiation chemistry of water and aqueous solutions

The radiation-chemical reactions occurring in water and aqueous solutions were an object of many investigations having been carried out during the last years in this country. This is caused first of all by the fact that water is used as a moderator and a coolant in atomic reactors; besides, in aqueous solutions many processes take place involved in the nuclear fuel production and isolation of nuclear reaction products. Moreover, behaviour of aqueous solutions under irradiation is analogous, in a considerable extent, to that of biological systems. That is why the study of the effects of ionizing radiation on the aqueous solutions can be assumed as basis for estimation the effects of radiation on living tissue.

Soviet research works cover a wide range of diverse questions of the radiation chemistry of water and aqueous solutions. The influence of a ionization density and dose

rate on the yields of radiolytic conversion in the aqueous solutions, the role of direct action of radiation on dissolved substance, the role of excited molecules of water in radiolysis processes, dependence of the yields of molecular products of radiolysis on concentration of solution were ascertained. Radiation-electrochemical processes and the influence of irradiation on corrosion behaviour of metals and some other questions were an object of a number of investigations.

At present is generally accepted that under the action of radiation on water atoms H and radical OH, as well as molecular hydrogen and hydrogen peroxide are generated as primary products of the radiolysis. These intermediate products interact further with the dissolved compound. In the case of the diluted aqueous solutions it is possible in this way to explain the character and the yield of the radiolysis products and, in some cases, the radiolysis kinetics also. Based on this conception systematic investigations are carried out in the USSR. [V.Yu.Filinovsky and Yu.A.Chizmadzhev¹⁹ have made calculations concerning the dependence of the molecular products yield in the case of the radiolysis of water under the action of radiations with high ionization densities in the presence of scavengers. Two cases of atoms H and radicals OH distribution during water radiolysis have been considered: 1) both radicals are in a track column with the diameter ~ 8 and 2) atoms H have more diffusive distribution ($\sim 100 \text{ \AA}$).

B.V.Frehler et al.²⁰ have compared the rate of radiation-chemical decomposition of hydrogen peroxide with the

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most reliable data available in the world literature concerning the radiolysis of water under the action of γ -radiation of cobalt-60. The authors have confirmed the applicability of hypothesis about the constancy of yields of radiolysis products of water as well as the adequacy of the law of homogeneous kinetics to the case of radiation chemical processes in diluted aqueous solutions.

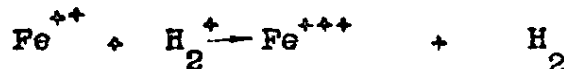
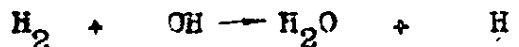
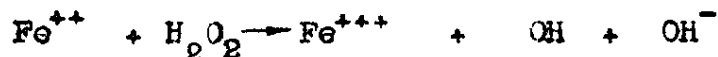
In an other paper B.V. Ershler²¹ basing on the model of irradiated solution in which free radicals and molecular products are distributed homogeneously in the total irradiated volume, has considered general regularities of the radiolysis, for the cases wherein this model is applicable. Proceeding from the assumption that radiolysis products yields of water are constant values and that in the solution only bimolecular reactions proceed, the author has considered the effects of radiation intensity on the dependence of yield upon concentration. Two criteria for the adequacy of this model have been found. In the case of stationary state, the increase of intensity from I_1 to I_2 displaces the curve representing the dependence of a logarithm of concentration of one of radiolysis products upon a logarithm of concentration of other product, along the coordinate axes by a segment which is equal to $\Delta I^{\frac{1}{2}}$, the shape of the curve being unchanged. If stationary state is not yet achieved, the variation of intensity leads to displacement by the same value $\Delta I^{\frac{1}{2}}$ along the abscissa of the curve representing the dependence of the radiation yield G of one product with logarithm of concentra-

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tion of another. Radiolysis of the solutions of hydrogen peroxide ²⁰ is an example of such a regularity.

It is known that increase of concentration can bring the conditions in which the dissolved compound would interact not only with free radical distributed in whole volume of solution but also with those in the points of high ionization density, competing thus with recombination reaction of radicals and reducing the molecular product yield. In this connection the investigations of P.I.Dolin with collabor., N.A.Bakh with collabor., M.A.Proskurnin with collabor., are of considerable interest. Examining the nitrate systems ²²⁻²⁴, as well as the aqueous solutions of potassium bromide ²⁵⁻²⁶, it has been found that a substantial part of molecular hydrogen originates from the recombination of atoms H. For instance, decreasing of magnitude of $G(H_2)$ till some hundredths of molecules per 100 electron-volt with the increasing NO_3^- -ions concentration has been found ²²⁻²⁴.

From the point of view of elucidating the mechanism of radiolytic oxidation of Fe^{++} -ions in diluted aqueous solutions of considerable interest is the work of V.N.Shubin and P.I.Dolin ²⁷, in which the effects of a pressure of hydrogen above the solution on the yield $G(Fe^{++})$ is investigated. It was found that variation of the pressure of hydrogen in the range from 1 to 180 atm. does not exert an appreciable influence on system concerned. [A mechanism has been suggested for this case which includes the following reactions:



The results obtained confirm the hypothesis according to which in deaerated solutions atoms H take part in oxidation of ions Fe^{++} , directly or by means of formation of the ions H_2^+ .

It is known the yields of radical and molecular products of water radiolysis are dependent on the magnitude of linear energy transfer, i.e. on kind of radiation. Although a number of soviet investigations hitherto carried out in this topic is not large, they are of a certain interest. A.M. Kabakchi et al. ^{28,29} has investigated effects of γ -radiation of cobalt-60, β -rays of phosphorus-32 and α -particles of plutonium-239 on aqueous solutions of nitrates in various concentration. Radiation-chemical yield of NO_2^- , according to the authors mentioned is dependent on the kind of the radiation. For instance, under the action of α -radiation of $\text{Pu}^{239} \text{G}(\text{NO}_2^-)$ is considerably less, than that in the cases of γ -rays of Co^{60} and β -particles of P^{32} .

Z.V. Epshova and M.V. Vladimirova ³⁰ have studied the action of alpha-particles of polonium on 0.8N aqueous solutions of H_2SO_4 . It has been found that the initial yield of hydrogen peroxide (1.2 molecules per 100 ev) is independent on

concentration of polonium dissolved in the range of specific activity from 0.1 to 12 millicuri per ml, concentration of H_2O_2 tending to its limit value. For 0.8 N H_2SO_4 the equilibrium limiting value of the H_2O_2 concentration amounts $5-3 \cdot 10^{18}$ molecules per ml.

①
1 - action of protons
2 - ... of γ -rays
Co

S.A. Brusontseva and P.I. Dolin³¹ have investigated the action of protons with the energy 660 Mev on aqueous KBr solutions. The linear energy transfer of the radiation mentioned is nearly to that of 1 Mev electrons. The work has demonstrated that the radiation-chemical phenomena are defined solely by the magnitude of the linear energy transfer. Thus the yields $G(Fe^{+++})$ obtained in the case of aqueous ferrous sulphate solution and $G(H_2)$ obtained for KBr solutions of various concentration (Fig. 1) have been found by the mentioned authors to be approximately equal to the corresponding values obtained under action of γ -radiation of Co^{60} .

Fig. 1.

②
1 - sol. of Fe^{+++}
2 - sol. of Co^{+++}
3 - sol. of Co^{+++} from mixture of salts
The

A.K. Pikaev and P.Ya. Glazunov³²⁻³⁷ have studied radiolytic transformations in aqueous solutions of several inorganic compounds at high dose rates. The latter have been achieved by means of pulsed electron radiation; the electron energy has been 0.8 - 1.0 Mev; the pulse duration - 5 μ sec. The radiolytic conversions in aqueous solutions of ferrous sulphate and ceric sulphate, of the mixtures of Ce^{+++} and Tl^+ sulfates and also Ce^{+++} and Ce^{++} sulphates have been investigated. The Fig. 2 indicates the dependence of $G(Fe^{+++})$, $G(Ce^{+++})$ in the absence of Tl^+ and also $G(Ce^{+++})$ in the

presence of Tl^+ upon dose rate, obtained by the authors. As one can see from the Fig. 2, the appreciable variation of yields takes place at the high dose rates up from about 10^{21} ev/ml. sec. For instance, $G(Fe^{+++})$ decreases with increase of the dose rate, whereas $G(Ce^{+++})$ under the same conditions increases. This is caused by the fact that at the dose rates up from $\sim 10^{21}$ ev/ml. sec. and higher the processes originated by overlapping of ionizing particle tracks begin to play a significant part, changing the yields of radiolysis products of water $G(H)$, $G(OH)$, $G(H_2)$ and $G(H_2O_2)$.

Fig. 2.

In the papers mentioned above³²⁻³⁷ it has also been observed that at high dose rates the importance of competition between radical-radical and radical-solute reactions is augmented. The Fig. 3 shows the dependence of the yields of radiolytic conversion in several systems upon the concentration of dissolved substance at high dose rates of radiation, found in above mentioned works.

Fig. 3.

The mechanism of radiolytic transformations in concentrated solutions is a problem of to-day. In this case not only the effects of radiation caused by the action of water radiolysis products on the dissolved substance take place, but also direct action of radiation on it is involved. A.M. Kabakchi is one of the first investigators having proposed the conception of the direct action³⁸. He has shown that in the radiolysis of aqueous chloride solution molecular

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chlorine is formed, the yield of which increases in proportion to increasing solute concentration independently of the kind of radiation or the cation nature.

A different point of view has been suggested by M.A. Proskurnin et al.^{14,23,24,39-43}. According to their hypothesis the high concentration gives possibility to radicals originated not only from ionized molecules of water, but also from excited molecules to be involved in the radiation-chemical reactions. In Fig. 4 the dependence found by the authors mentioned above²⁴ is shown, between the yield $G(\text{NO}_2^-)$ and concentration of NaNO_3 solution. The radiation yield $G(\text{NO}_2^-)$ increases with augmentation of NaNO_3 concentration reaching a constant value in the region $5 \cdot 10^{-4}$ - 10^{-2} M. The authors have suggested that existence of this slightly sloping segment of the curve can be explained by involving of practically all the H-atoms formed in the reaction with nitrate-ions. In the more concentrated solutions the yield $G(\text{NO}_2^-)$ increases again, and for the 1-6 M solutions remains constant. According to the authors²⁴ the increase of the yield $G(\text{NO}_2^-)$ in the concentrated solutions is caused by involvement in the process of the H-atoms originated from both the ionized and excited molecules of water.

1- in absence of
2- in presence of
4

Fig. 4.

It is M.A. Proskurnin who has discovered the radiation sensibilization phenomena described below. If in a solution one adds a substance capable to interact easily with one of the radical radiolysis products of water, there are

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created conditions in which another radicals are more completely involved in radiolytic conversion. In the case of nitrate system according to ^{14,39,44} such substances are glycerol and glucose. Being active acceptors of OH-radicals these promote $G(NO_2^-)$ to be higher.

The curve 2 in the Fig. 4 represents the dependence of $G(NO_2^-)$ on concentration of $NaNO_3$ solution in the presence of glycerol. Here the yield $G(NO_2^-)$ in the case of highly concentrated solutions reaches a value of ≈ 6 ions/100 ev, what implies involving of all water radiolysis products in the reaction with dissolved substance.

Recently, M.A.Proskurnin et al. ⁴⁵ have proposed the hypothesis according which there are two kinds of excited molecules of water differing in level and type of excitation. This hypothesis can explain the existence of three limiting values of the radiolysis yield of dissolved substance in dependence in various conditions of radiolysis. In the case of nitrate system, as it was mentioned above, the limiting values of $G(NO_2^-)$ are equal to 2, 4, and 6 ions/100 ev.

Radiolytic transformations in concentrated aqueous solutions have been investigated by a number of another soviet scientists. The work of L.T.Bugaenko and V.N.Belevsky ⁴⁵ dedicated to the problem of direct action of radiation on the concentrated perchloric acid aqueous solutions is of a certain interest.

As it has been found by A.A.Balandin, V.I.Spitsyn et

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al.⁴⁷, under the effects of irradiation on aqueous solutions of a several complex salts of platinum the precipitation of metallic platinum takes place, product having a higher catalytic ability in the low-temperature reaction of cyclohexene hydrogenation. Palladium black prepared on radiation-chemical method differs, according to the same authors⁴⁸, by its catalytic properties from the material prepared in conventional way.

Radiolytic transformations in aqueous solutions of plutonium have been examined by H.A.Bakh and collab.^{49,50} Several papers of soviet authors are devoted to radiolysis of aqueous solutions of uranium^{51,52} and americium. [V.G.Firsov and B.V. Ershler⁵¹ examining radiation-chemical reactions in aqueous solutions of uranium (IV) have found that under the action of γ -radiation of Co^{60} radicals OH and hydrogen peroxide are responsible for oxidation of U^{+4} -ions. As concentration rises, the oxidation yield at first increases and subsequently is lowered. In the presence of oxygen G (UO_2^{++}) is significantly more (16 eq/100 ev) than that in the degassed solutions. The authors have deduced the equation describing the dependence of G (UO_2^{++}) upon U^{+++} concentration, the ratio of the rate constants of the three reactions ($\text{U}^{+4} + \text{OH}$, $\text{H} + \text{OH}$ and $\text{H} + \text{H}$) being involved.

G.N.Yakovlev with collab.⁵³ examining the effects of inherent α -radiation of Am^{241} on the valency state of americium in the aqueous solution have found that radiation-chemical reduction of AmO_2^{++} ions in a considerable degree

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is dependent on acidity of the solution as well as on nature of the acid. For example, in the concentrated solution of perchloric acid the yield $G(\text{AmO}_2^{++})$ is appreciably lower, than that in diluted solutions. The reduction of NpO_2^{++} ions in aqueous solutions induced by electron radiation⁵⁴ is also dependent on the factors mentioned above. It is of an interest that, from radiation-chemical point of view, the pentavalent neptunium is more stable than other valency states.

Radiation electrochemical processes in aqueous solutions have been an object of several works of soviet authors. N.A.Bakh et al^{22, 55} have examined change of oxidation-reduction potential of several compounds in aqueous solutions under action of ionizing radiation. Extensive investigations of radiation electrochemical processes have been carried out by V.I.Veselovsky and collab.⁵⁶⁻⁶¹. That in the works of the latter it has been discovered that the potential of the platinum electrode in irradiated 0,8 N sulfuric acid solution saturated with nitrogen reaches a value closely approximating to the reversible hydrogen potential and the potential of the gold electrode becomes equal to -0.95 volt.

D.V.Kokoulina, P.I.Dolin and A.N.Frumkin⁶², examining behaviour of smooth platinum electrode in the solution of sulfuric acid in wide range of doses absorbed and dose rates, have been proved that the potential of platinum electrode in irradiated 0.8 N sulfuric acid is controlled by the molecular radiolysis products of water accumulating in solution, i.e. by hydrogen and hydrogen peroxide. The radical products of

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radiolysis in this case do not play any appreciable part in potential establishment on platinum. A similar conclusion has been drawn by S.D.Lovina and T.V.Kalish⁶³ from an examination of the behaviour of nickel electrode under irradiation. [Examining the oxidation-reduction reaction $\text{Fe}^{++} \rightarrow \text{Fe}^{+++}$ under irradiation P.I.Dolin and V.I.Duzhenkov⁶⁴ have proved the potential possibility of utilization the products of oxidation and reduction in aqueous solutions for the purpose to transform energy of radiation into electrical energy. In other words, the possibility of constructing radiation-galvanic cell has been proved. Another solving of this problem has been stated by V.J.Veselovsky et al.⁵⁹. They have employed the Pt and Au electrodes having selective properties with respect to oxidizing and reducing agents formed in solutions under irradiation.]

There are a number of soviet works examining the influence of ionizing radiation upon the corrosion behaviour of metals in various media. N.D.Tomashov, A.V.Byalobzhesky et al.⁶⁵ have studied the effects of electron radiation on corrosion of iron, stainless steel and aluminium in sodium chloride solutions. A.V.Byalobzhesky^{66, 67} has examined corrosion of metals under irradiation in air. The corrosion of several metals under irradiation (by fast electron beam, γ -rays of Co^{60} , X-rays) has been found by him to be appreciably accelerated by ionizing radiation. The metals examined can be arranged in the following consequence: iron - copper - zinc - aluminium, the corrosion stability increasing. It has been suggested in the works mentioned above that the corrosion intensification

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under irradiation is caused by formation of radiolysis products of oxygen, water and nitrogen in the air.

68,69

I.L.Rosenfeld and E.K.Oshe have examined the effects of electron radiation on electrochemical activity in various media of zirconium and titanium covered with oxide films having semi-conductor properties. [Diminution of anode and cathode reaction overvoltage and increasing of rate of these reaction have been found. The effect discovered is reversible: stopping of irradiation leads to return of overvoltage and rates of anode and cathode reactions to values closely approximating to original ones. Another phenomenon of an interest discovered by the authors, is the fact that under irradiation behaviour of metals covered with semi-conductor films of p-type and of n-type with respect to anode process is quite different. With respect to cathode reaction such a difference is not observed.]

The corrosion behaviour of several metals under irradiation has also been studied by Ya.M.Kolotyrkin et al. 41, 70. For example 41, they have investigated the effects of γ -radiation of Co^{60} on electrochemical properties and corrosion of steel, nickel and platinum in sulfuric acid. It was established, in the case of steel and nickel, that effect of irradiation is equivalent to anode polarization. The authors have confirmed the conclusion by V.J.Veselovsky with collabor. 56-61 about establishment in sulfuric acid the platinum electrode potential closely approximating a potential of reversible hydrogen electrode.

3. Radiation chemistry of simple inorganic molecules

A number of works by soviet authors is dedicated to study the radiation-chemical reactions of simple inorganic molecules. The attention to these investigations has been attracted, first of all, owing to the fact that the examinations of such reactions allows, more successfully than in cases of other compounds, to correlate the yields and kinetics with ionization and excitation potentials, dissociation energy and other parameters of irradiated material as well as to study the effect of phase state on radiolysis and to correlate radiation-chemical and photochemical processes.

The most complete investigation in this topic accomplished by soviet chemists is radiation chemical oxidation of nitrogen with the oxygen. S.Ya.Pshezhetsky and M.T.Dmitriev^{71,72} have examined kinetics and mechanism of oxidation of nitrogen under the action of electron impact. [Nitrogen pressure has been varied from 10^{-2} to 10^{-3} mm Hg, electron energy - from units of electron-volts to 200 Kev.] Formation of N_2^+ -ions appears to be an intermediate stage of the reaction. Kinetics of the reaction is described by an equation of the second order, activation energy being in the range 2-7 kcal/mol. [Later, M.T.Dmitriev and S.Ya.Pshezhetsky⁷³ have carried out work on oxidation of nitrogen induced by γ -radiation of Co^{60} under pressures up to 150 atm. and at temperatures 15-25° and at 150°C. It has been observed that increasing of pressure from 1 mm Hg to 760 mm Hg lowers the oxidation reaction yield, but at the further increasing of pressure the

yield increases, reaching the magnitude of 5-6 molecules of NO_2 per 100 ev at 150 atm. The yield of N_2O at 3-50 atm at 150°C is 2.5-3.5 mol/100 ev. The dependence of the reaction rate on composition of mixture obeys to an equation of the second order. A deviation from the equation of the second order has been observed for the dependence of reaction rate and yield on the pressure, because of recombination of ions formed under irradiation.

Recently M.T.Dmitriev and S.Ya.Pshezhetsky⁷⁴ have examined the transformation occurring in nitrogen dissolved in water under action of γ -radiation of Co^{60} and a beam of fast electrons. It has been found that nitrogen dissolved in water under irradiation is fixed in form of nitrate, nitrite and ammonia. The yield of the reaction is dependent on a composition of mixture of gas dissolved and its pressure. For instance, the yield of nitrogen fixed is 0.09-0.18 at 1 atm. and 1.0-1.4 atoms at 150 atm. per 100 electronvolts of radiation energy absorbed.

S.Ya.Pshezhetsky et al^{75,76} have also studied the formation of ozone in liquid and gaseous oxygen under action of γ -radiation of Co^{60} and fast electron stream. Excited molecules of oxygen have been proved to play an important role in the reaction. The radiation-chemical yield of O_3 is 12-15 molecules/100 ev in the case of liquid phase and 1.5 molecules/100 ev for the gas.

Hydrazine is formed under the action of fast electron

beam on liquified ammonia⁷⁷. The latter process is characterized by stationary hydrazine concentration owing to the equilibrium between rates of direct and reverse reactions, the yield being 1.0-1.2 molecules/100 ev.

It has been studied the kinetics of hydrogen peroxide decomposition depending on its concentration in aqueous solution under action of γ -radiation of Co^{60} , ultraviolet light as well as the analogous dependence for the rate of the thermal decomposition⁷⁸. The rate of the reaction as the concentration increases has been found to have always a maximum. It has also been observed that the rate of the radiation-chemical reaction is proportional to square root of radiation intensity. The activation energy of the radiation-chemical reaction is 6.5 kcal/mol, that of the photochemical reaction being 8-9 kcal/mol. The yield of the radiation-chemical reaction is dependent on temperature. Dependence of a degree of electrolytic dissociation of NO_2 -radicals on the concentration of the solution is proposed in the paper for explanation of kinetics of the reaction of H_2O_2 decomposition.

Several papers of soviet authors deal with investigation of effects of ionizing radiation on solid substances.

V.I.Spitsyn et al.⁷⁹ have examined decomposition of solid complex compounds of platinum under the action of electron radiation. In these cases formation of free metallic platinum was sometimes observed. [The magnitudes of the initial yield of metal are represented in the table 1.] The data of the table show that a degree of decomposition of the

-20-

complexes is dependent on nature of the salt and space isomerism. For instance, $\text{trans-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ has lower radiation-chemical stability, than that of the cis- isomer. As it is obvious from the Fig. 5 and Fig. 6, the degree of decomposition of the complex salts remains unchanged at the high integral irradiation doses. In these conditions the process of re-oxidation of free metallic platinum by atomic chlorine brought about with radiation-chemical decomposition of the compounds concerned has apparently a significant part.

Table 1

The initial yields of free metallic platinum
at irradiation of complex compounds

Compound	Initial G (Pt), atom/100 ev.
$\text{K}_2[\text{PtCl}_4]$	0.018
$(\text{NH}_4)_2[\text{PtCl}_4]$	0.143
$(\text{NH}_4)_2[\text{PtCl}_6]$	0.090
$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$	0.047
$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]\text{-cis}$	0.036
$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]\text{-trans}$	0.338

M.A. Proskurnin et al. have investigated the effect of γ -radiation of Co^{60} on solid NaNO_3 and KClO_4 as well as on crystalline hydrates of nitrate salts as paper is of a certain interest describing the effect of dose rate of γ -radiation of Co^{60} in the region of $0.2 \cdot 10^{16}$

FIG. 5.
FIG. 6.

to $4.1 \cdot 10^{16}$ ev/ml. sec. on the radiolysis product yields of several crystalline hydrates of nitrate salts. It has been proved that a minimum on the curve expressing the dependence of $G(\text{NO}_2^-)$ upon dose rate is a characteristic feature for all crystalline hydrates examined, the position of the minimum being determined by nature of the cation. The crystalline hydrates are more sensible to the action of γ -radiation than the corresponding anhydrous salts.

V.V.Boldyrev et al.⁸⁴ have considered the effect of preliminary irradiation on the rate of thermal decomposition of silver oxalate contaminated with cadmium. The preliminary irradiation with γ -rays of Co^{60} brings about an intensive acceleration of the subsequent thermal decomposition of pure silver oxalate. Thermal decomposition of the salt containing traces of cadmium is accelerated, too, but in a considerably smaller degree. On an opinion of the authors the phenomenon is caused by the formation in the presence of cadmium in crystal lattice additional number of cation vacancies, which can trap positive holes or argentine cations from interstitials.

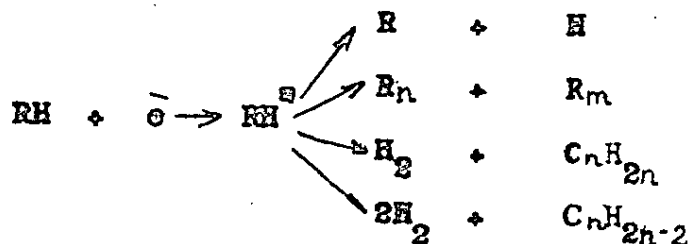
4. Radiation chemistry of organic compounds

The reactions of organic compounds induced by ionizing radiation are objects of research work of a number of soviet investigators. The works are carrying on in several directions.

A.V.Topchiev and L.S.Polak with collaborators⁸⁵⁻⁹² are carrying out the systematic investigation of the effects of

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γ -radiation of Co^{60} and of fast electron beam on hydrocarbons in gaseous, liquid and solid phases. Based on experimental data the following possible types of initial radiolysis reaction of normal alkanes have been suggested in their papers.



Examination of ESR-spectra of irradiated at 77°K in frozen state n-heptane indicated the occurrence of free alkyl radicals and also of H-atoms but in a smaller number. It has been proved that these radicals can be kept at low temperature over a long period of time.

It has been found by the authors mentioned above as well as by foreign authors that the total yield of the radiolysis products of hydrocarbons at room temperature is about 10 molecules/100 e.v., the predominant process being dehydrogenation. The examination of the radiolysis of n-heptane is the most detailed. At irradiation of n-heptane in ordinary conditions the gaseous radiolysis products contain about 80 % of hydrogen. The rest of 20 % includes saturated and unsaturated hydrocarbons.

In the series of soviet investigations in radiation chemistry of hydrocarbons those of radiation thermal cracking of hydrocarbons are of a significant interest⁹⁰⁻⁹². It has been found that at simultaneous action of radiation and

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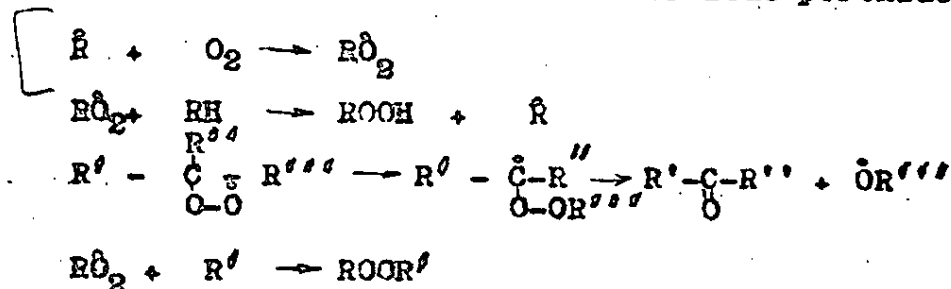
heat the chain reaction of cracking occurs, initiation of the reaction being caused by radiation, while propagation of the reaction being maintained on account of heat energy. For instance, as one can see in Fig. 7, irradiation of n-heptane at elevated temperatures leads to the sharp increasing of yields of hydrocarbon products of radiolysis. Moreover, among the products of radiolysis an increase in unsaturated hydrocarbons content is noted (Fig. 8). One can suppose that the radiation thermal cracking of hydrocarbons should be a perspective method as regards to uses of nuclear radiation in the practice purposes.

Fig. 7.

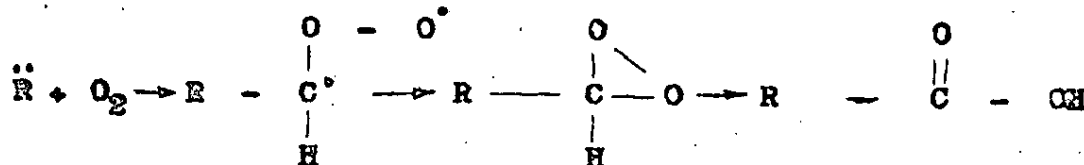
Fig. 8.

Another branch of radiation chemistry of organic compounds developed by the soviet scientists is study of radiation induced oxidation processes in organic systems. N.A. Bakh with collabor. ⁹³⁻⁹⁹ [are carrying on the most methodical research in this topic, under utilization of diverse types of radiation: X-rays, γ -radiation of Co^{60} , fast electrons, mixed radiation of a nuclear reactor. Authors mentioned above] ^d are first to have found ⁹³⁻⁹⁴ that under irradiation of liquid hydrocarbons (heptane, isooctane, benzene, cyclohexane, etc.) saturated with oxygen the oxidation of the hydrocarbons at room temperature occurs generating peroxides, carbonyl compounds, alcohols, acids, etc., the formation these compounds being simultaneous right from start of irradiation. In the case of hydrocarbons in ordinary conditions the reaction of oxidation is not chain reaction. Ethyl alcohol and acetone, molecules of which contain more movable atoms of hydrogen are oxidized on the chain mechanism with short chain. The

following scheme suggested by N.A.Bakh, for explanation of radiation induced oxidation is based on the supposition that peroxide radicals can be formed by addition of oxygen molecules to the free hydrocarbon radicals. The simultaneous formation of the radiolysis products is caused by occurrence of some parallel reactions of the peroxide radicals of one type or by simultaneous formation of the various peroxide radicals:



Biradical \dot{R} , which can also arise under irradiation of hydrocarbon, interacting with oxygen gives a molecule of acid:



Oxidation of methane by oxygen at room temperature under action of fast electron beam has furthermore been studied by B.M.Mikhailov et al. ¹⁰⁰⁻¹⁰². They have not observed any chain reaction of oxidation, too.

N.A.Bakh as well as M.I.Proskurnin are carrying out investigations of radiation induced oxidation of organic compounds in aqueous solutions. In this case oxidation is mainly caused by interaction of radiolysis products of solvent with dissolved substances. Hence the oxidation can here take place even in absence of molecular oxygen.

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M.A. Prokurnin et al.¹⁰³⁻¹⁰⁴ have conducted a detailed examination of radiation chemical oxidation of benzene into phenol in aqueous solution. They have observed an interesting phenomenon: the yield of phenol in presence of Fe^{++} -ions can increase 3 times as against the ordinary yield and amounts 6 molecules/100 ev. It has been also examined radiation induced oxidation of chlorobenzene in aqueous solutions¹⁰⁵. It has been proved hydrolysis of chlorobenzene plays an important part in the radiolysis.

M.A. Bakh et al.¹⁰³ have investigated oxidation of ethyl and isopropyl ether in aqueous solutions under action of X-rays and fast electron beam. In the presence of oxygen the process of their oxidation proceed by chain mechanism. Products of the reaction in both two cases are peroxides (the yield is about 20 molecules/100 e.v.), carbonyl compounds (the yield is about 25 molecules/100 e.v.), alcohols and acids.

At high temperatures, as it has been shown by N.M. Emanuel¹⁰⁷ and M.A. Prokurnin et al.^{108,109}, chain oxidation of hydrocarbons under action of radiation takes place. For instance, it has been observed that under action of γ -radiation paraffin in the presence of oxygen is effectively oxidized at 127-130° C giving fatty acids. The process of oxidation proceed by the degenerated chain-branching mechanism.

Recently V.A. Bakh and Tung Tyan'-chzhen'¹¹⁰ have examined the temperature dependence of radiation-chemical oxidation of n-heptane and n-octane. For both hydrocarbons studied there are two regions of temperature dependence of the yield

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of oxidation products. At the temperature below 70°C small yields and independence on temperature are observed. At temperature above 70° the yield of radiolysis products sharply increases with temperature, reaching in the case of peroxides the value of 30-40 molecules/100 e.v. In the case of radiation induced oxidation of n-alkanes as it has been shown in the paper mentioned, interference of chain and ordinary reaction mechanism is a distinctive feature. The temperature, at which the chain reaction are initiated, is dependent on nature of irradiated compound.

A number of soviet scientists are studying the effects of ionising radiation on mixture of organic compounds. The work of Kh.S. Bagdasarian with collabor. ¹¹¹⁻¹¹³ is of a considerable theoretical interest. Examining γ -radiation induced decomposition of benzoyl peroxides in various solvents the authors mentioned above have found that in benzene solutions effective transfer of excitation energy from benzene molecules to peroxide molecules occurs, increasing in a significant degree the radiation chemical yield of its decay.

[For reaction studied excitation energy transfer is observed if molecules of both the constituents of the solution have aromatic groups. For example, in cyclohexane and ethyl acetate solutions the energy transfer from solvent does not occur, and a chain reaction of decomposition of peroxide is induced by radicals formed under irradiation of solvents. However any simple correlation between structure of molecules and its ability to accept the excitation energy does

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not exist ¹¹³. For example, azobenzene does not accept the excitation energy, although its molecules contain two phenyl rings conjugated with double bond. Some compounds being active acceptors of the energy are negligibly capable or incapable at all to use the energy for chemical transformation. For instance, such a compound is phenylazotriphenyl methane, which does not dissociate on radicals, under action of excitation energy accepted in spite of the fact that this reaction occurs easily under the action of heat.

In the recent paper of Kh.S. Bagdasarian et al. ¹¹⁴ examination of radiolysis of diluted benzene solutions of organic disulphides containing aromatic and aliphatic substituents has been described. Due to the radiation energy transfer from the solvent to the dissolved compound, the yields of decomposition of disulphides have been found to be sufficiently more high than the yield being expected in the case when all amount of energy absorbed by them would be spent completely for their decomposition. The energy transfer efficiency has been found in the work referred to be dependent on the nature of the disulphide. Thus, diphenyldisulphide and dibenzoyldisulphide are approximately identical energy acceptors, while accepting capacity of dibenzoyldisulphide is half of that of the former. Aliphatic disulphides (diethyldisulphide, dicitryldisulphide) manifest more low decomposition yields than those of aromatic disulphides, due to the considerably smaller intermolecular energy transfer efficiency.

A number of papers have been published by soviet authors, dealing with radiation-chemical halogenation, amidation, etc. P.V.Zimkov et al.¹¹⁵ have examined effects of γ -radiation of Co^{60} on chlorination reaction of benzene in the temperature region from -80 to $+40^\circ \text{C}$. The radiation chemical chlorination of benzene has been found to proceed with the yield of 400000 molecules/100 e.v., the resulting material having elevated content of high-toxical γ -isomer of hexachlorocyclohexane in comparison with industrial product obtained by photochemical method.

The effects of ionizing radiation on mixtures of benzene - ammonia, benzene-carbon tetrachloride, and benzene-carbon tetrachloride with compounds containing^B fluorine have been examined by A.M.Zimin with collabor.¹¹⁶⁻¹¹⁸. In the mixture of benzene and ammonia under γ -irradiation aniline with a small yield is formed. In the case of the benzene-carbon tetrachloride system formation of monochlorobenzotrichloride has been observed (parallel with some other radiolysis products). In the mixtures of CCl_4 with inorganic fluorides and of benzene with simplest fluorocarbons fluorination of CCl_4 and of benzene takes place.

P.V.Dzhagatsepanian et al.¹¹⁹ have studied chlorination of silicon-organic monomers and polymers under effects of γ -radiation. In another paper of the authors mentioned radiation chemical sulphochlorination and sulphoxidation of paraffins as well as some polymers are described. 120

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Researches on working up of radiation-chemical methods of organic synthesis are carrying out in this country.

K.A.Kocheshkov et al.¹²¹ have proposed the radiation-chemical method of preparation of tin-organic compounds. V.I. Spitsyn et al.¹²² have worked out radiation chemical synthesis of butyl ether of phosphonitryl chloride. The reaction proceeds with a good yield under action of fast electron beam on solution of phosphonitryl chloride in n-butyl alcohol.

Radiation-chemical transformations in dyes and substances of biochemical interest are also being studied by soviet chemists. [I.V.Vorochinsky¹²³ has examined the synthesis and transformations of leuco-compounds of the dyes under action of γ -radiation of Co⁶⁰ as well as the effects of γ -radiation on synthesis of indophenol¹²⁴. In a number of soviet papers¹²⁵⁻¹²⁸ the radiolysis of methylene blue in aqueous solution is described. M.A.Prokurnin et al.¹²⁹ examined radiolytic decoloration of indigo carmine solutions. A large number of investigations deals with the effects of ionizing radiation on substances of biological interest, i.e. proteins¹³⁰, aminoacids¹³¹, carbohydrates¹³², animal fats¹³³, etc. Radiolysis of protoporphyrin has been examined by I.V.Vorochinsky¹³⁴.

5. Radiation polymerization

Radiation polymerization, at present, ranks rather high among the problems to be solved for the uses of ionizing radiation in the practice. This is called forth by the fact

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that in the majority of cases the radiation induced polymerization as it has been shown in a number of papers including some papers of soviet authors¹³⁵, proceeds by a chain mechanism, the process being initiated by free radicals arising under irradiation of the monomer.

Researches in radiation polymerization are carried out in many countries. In the USSR the work in this field realize S.S. Medvedev^{135, 136}, Kh. S. Bagdasarian^{137, 138}, A.D. Abkin¹³⁹⁻¹⁴¹, B.L. Tsotlin¹⁴² and other soviet investigators.

Among the recent investigations on this topic that of B.L. Tsotlin, V.A. Sergeev, S.R. Rafikov, V.V. Korshak, P.Ya. Glasunov and L.D. Bubis¹⁴², concerning radiation chemical polymerization of methyl-methacrylate, is of a considerable theoretical and practical interest. In the presence of air the methyl methacrylate has been found not to be polymerized under action of ionizing radiation. However, spontaneous polymerization of the irradiated material proceeds at room and lower temperature to the high degree of the conversion, after the access to the material of the ambient air has been stopped. Investigations of the polymerization kinetics of irradiation and at various temperatures, indicated that, in the first degree of approximation, the process by its character is identical to polymerization process of peroxide type and another types of radical polymerization. On opinion of the authors of the paper cited, the polymerization process is initiated by products of radiation chemical oxidation of methyl methacrylate (probably peroxides formed by interac-

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tion of primary free radicals with oxygen). Being high active these products create possibility the low-temperature polymerization to be executed. The feature of interest is the fact the curves representing polymerization kinetics are in this case more smooth in comparison with those in the case of polymerization by Benzoyl peroxide. The "gel-effect" in the processes described take place when a considerably more high degree of conversion is achieved and the ratio of the maximum reaction rate in the self-acceleration stage to the initial rate is of smaller value. The curves representing the dependence of ratio of polymerization rate in a given moment to the initial rate upon relative duration of the process are shown in Fig. 9.

⑨
1 - previous non-steady state
2 - in a steady state
Fig. 9. Dependence of the ratio of polymerization rate in a given moment to the initial rate upon relative duration of the process.

Recently the paper of S.S. Medvedev, A.D. Abkin with col-lab. 145 about polymerization of ethylene under γ -radiation of Co^{60} was published. In this work the rate of radiation polymerization of ethylene in solution and in gaseous phase under various pressures (concentrations), as well as some properties of polymers formed have been examined. At a pressure 80 atm., temperature 25°C and dose rate 98 röntgen/sec polymerization of ethylene in heptane, cyclohexane, methyl alcohol and acetone proceeds with a rate 10 times exceeding the rate of the polymerization in gaseous phase at the same pressure. [In carbon tetrachloride tetrachloroalkanes with various molecular weight are formed. At the initial stages the process proceeds with acceleration, further the rate of the process being constant. The rate of the process is proportional

to irradiation dose rate in the power 0.3, while the radiation yield is ~~inversely~~ proportional to the dose rate in the power 0.7. The resulting polyethylene possesses higher density ($0.945-0.975 \text{ g/cm}^3$) and crystallinity than the high pressure polyethylene. Tensile strength of the polyethylene prepared by radiation-chemical method differs little from that of the high pressure polyethylene.

Kh.S. Bagdasarian, V.V. Voevodsky et al. ¹³⁸ have carried out investigation of graft-polymerization with irradiated ~~ed out investigation of graft-polymerization with~~ irradiated teflon. For elucidation of mechanism of the process a method of electron spin resonance has been employed.

Kh.U. Usmanov, U.N. Musaev, R.S. Tillaev ¹⁴⁴ have investigated the radiation chemical method of preparation graft copolymers in the systems polystyrene-acrylonitril and perchlorovinyl-acrylonitril. It has been observed in the case of polystyrene and acrylonitril that the reaction proceeds in a polystyrene film swollen in acrylonitril under radiation up to dose $1 \cdot 10^6 - 4 \cdot 10^6$ reentgon. Preparation of graft copolymers on the basis of perchlorovinyl and acrylonitril was accomplished by irradiation of a perchlorovinyl film (in presence of air) with the consequent treatment with acrylonitril.

As it has been mentioned, radiation polymerization in the most of cases proceeds by a free radical mechanism. However, recently it has been established that under certain conditions (e.g. ^{for example} at low temperature) polymerization under action of ionizing radiation can also proceed by carbonium-ion mechanism. Thus A.D. Abkin et al. ^{139, 141} have demon-

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 ✓✓
 treated this fact by copolymerization in the systems: isobutylene-vinylidene chloride, styrene-methyl methacrylate, isobutylene-styrene. Recently ^{140, 141} the results indicative of possibility for the reaction to proceed by a carb-anion mechanism have been obtained. Acrylnitril, which molecules contain an electronegative group, is polymerized under action of γ -radiation of Co^{60} in solvents containing nucleophilic substituents (e.g. triethylamine or dimethylformamide) but is not polymerized in the solvents containing electrophilic group (e.g. ethyl chloride). On the other hand, in ethyl chloride styrene is polymerized. [In the table 2 the data obtained by A.D. Abkin and collabor. are represented concerning polymerization of acrylnitril in a various solvents at temperature -78°C under effects of γ -radiation.

Table 2

✓ Polymer 105

Monomer	Concentration of monomer, mol/l	Polymerization rate (mol/l $\cdot 10^5$) in:			
		ethyl chloride	dimethyl formamide	triethyl-amine	in block
Styrene	2.0	1.95	no polymerization		
Acryl-nitril	3.5	no polymerization	0.97	0.67	0.21

✓
 If copolymerization of acrylnitril and styrene in dimethylformamid solution is carried out at -78°C , the resulting copolymers have found by authors mentioned, to be highly enriched by nitril component in comparison with the original mixture. All these data are indicative of possibility to

realize the carbonic mechanism of polymerization by the action of ionizing radiations.

Investigation of employment of ionizing radiation for preparation of inorganic polymers are begun by soviet scientists. Thus, V.I. Spitsyn et al.¹⁴⁵ have demonstrated the potential possibility of polymerization of phosphonitryl chloride under electron radiation. It is of interest that in this case polymerization proceeds only in presence of oxygen.

6. Effects of ionizing radiation on polymers

In the USSR first systematic investigations of effects of radiation on polymer materials were carried out by V.A. Kargin with collab.¹⁴⁶⁻¹⁴⁹ concerning, mainly, change of thermo-mechanical properties of irradiated materials. At present investigations in this field are being carried out by a number of soviet scientists, (S.S. Medvedev, L.L. Karpev, Ya.S. Lasurkin, B.L. Tootlin, N.A. Slevokhotova, A.B. Taubman).

V.L. Karpev et al.^{150, 151} studied effect of radiation on various polymer substances^{*}. They employed radiation of different kinds including α - and β -radiation of radon and products of its disintegration, γ -radiation of Co^{60} , fast electron beams, mixed irradiation of nuclear reactor. It was found that all polymers can be subdivided into two principal groups. The polymers of the first group are characterized by predominance of destruction processes, i.e. rupture of polymer chain. The polymers, in which under action

^{*} Researches in the field of radiation chemistry of polymers had been begun by V.L. Karpev in 1947.

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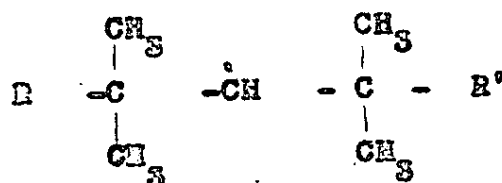
of radiation processes of cross-linking predominant, i.e. formation of chemical bonds between macromolecules, constitute the second group.

2
The evolution of polymers under irradiation was studied by V.L.Karpev et al. ^{150, 152} and some conclusions concerning mechanism of radiation chemical reaction in polymers were deduced. In the case of cross-linking polymers the major part of gas evolved is hydrogen. [Thus for instance, under irradiation of polyethylene the gas evolved contains 98,5 % of hydrogen. This can be confirmation of the suggestion that the cross-linking process passes through intermediate stage of formation free radicals by rupture of C-H bonds. Destruction of polymers is observed in all the cases when the main chain of macromolecule contains quaternary carbon atoms. Under irradiation of such polymers the evolving gas is impoverished in hydrogen and contains considerable amount of compounds resulting from detaching of side groups at quaternary carbon atom.]

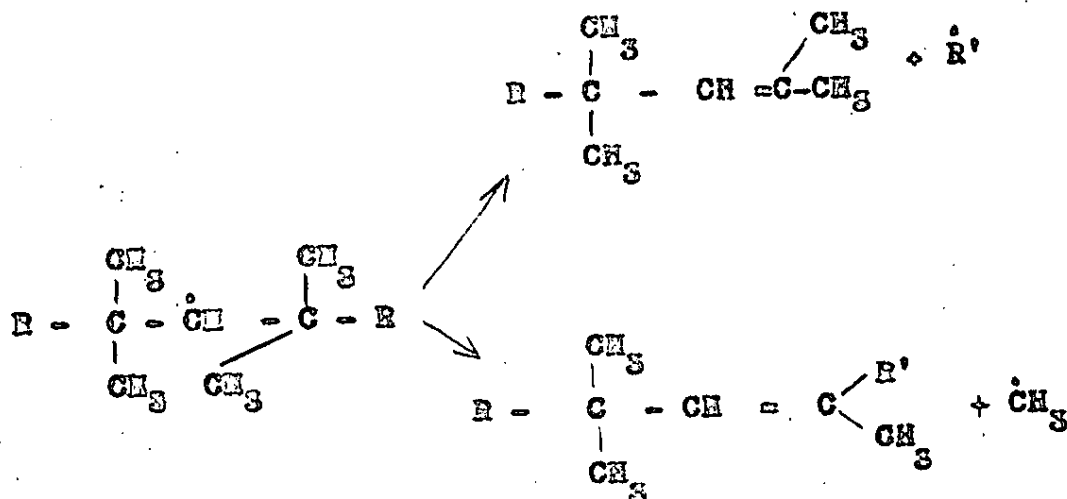
V
In their investigations V.L.Karpev and N.A.Slovenkhotova ¹⁵³⁻¹⁵⁵ employed widely spectral methods. By this technique it has been found in the case of polyethylene that irradiation results in gradual disappearance of vinylidene double bonds, which were present in the original material in a little amount, and formation of new double bonds of the trans-vinyl type (mainly conjugated). Formation of the double bonds is also observed in the case of destructing polymers. [In polyisobutylene formation of double bonds proceeds in all probability,

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by the following mechanism. By H-atom abstraction from secondary carbon atom the radical of the following type arises:



Because of steric hindrance this radical cannot form cross-link, and undergoes further destruction:



Examination of infra-red spectra has helped to discover the peculiarities of interaction of irradiation polymers with oxygen of the air. This process has been found to bring about formation of oxo-groups in the polymer. Another phenomenon of interest observed by V.L.Karpov et al.^{150,152,156} is destroying of crystallinity in polymers under effects of γ -radiation of Co^{60} or fast electrons. These processes were observed in the cases of polyethylene, guttapercha, co-polymer of vinyl chloride and vinylidene chloride, polytetrafluoroethylene and some other crystalline polymers.

V.L.Karpov, L.A.Blanckfeld et al.¹⁵⁷, by means of

measurements of infra-red spectra, absorption spectra and electron spin resonance spectra of irradiated polyvinylchloride have proved that the profound changes observed in this material under electron irradiation consist chiefly in splitting off hydrogen chloride and formation of double bond. On opinion of the authors, free radicals are responsible for change of colour in polyvinylchloride under effects of radiation. Their availability in the irradiated polymer has been proved by electron spin resonance method, their concentration being decreased with time progression. This decreasing is caused by recombination of the radicals in evacuated polymer and by interaction of the radicals with oxygen, resulting in formation of peroxide radicals if oxygen is available.

The papers of A.B.Faibman et al. ^{158,159} deal with problems of elucidating peculiarities of radiation destruction of polymers. They have examined the effects of electron radiation and high temperature on destruction of polytetrafluoroethylene, polymethylmethacrylate and polyethylene. The authors have obtained sharp change in rate of gas evolution under irradiation in narrow temperature region where melting (softening) of polymers is observed.

The phenomena of cross-linking in polymers are in focus of attention of soviet chemists since due to this process the most of polymers acquire the valuable properties. The mechanism of cross-linking in polyethylene has been examined by S.S.Medvedev et al. ^{160,161}. The temperature dependence of cross-linking in this material implies the cross-linking

-38-

being resulted by simultaneous detachment of two hydrogen atoms in a single primary act from two adjacent macromolecules.

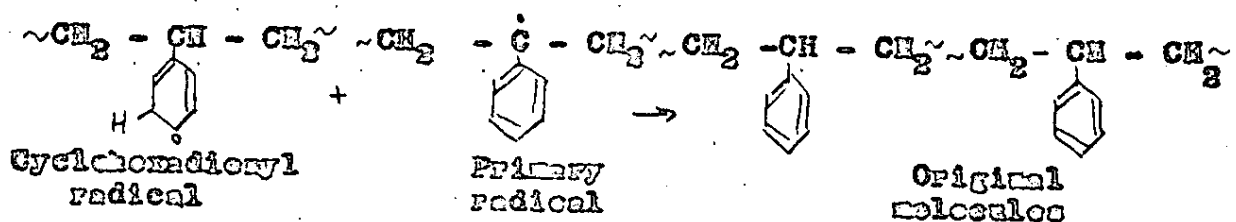
[V.V.Vorobeyko et al. ¹⁶² have examined by means of ESR-method the formation of free radicals in irradiated polyethylene. Radicals of two kinds (of alkyl and allyl types) have been observed in irradiated polyethylene. The stability of these radicals is different implying the different mechanism of their recombination. On opinion of the authors the recombination of radicals accumulated in course of irradiation must play an important part in process of cross-linking in polyethylene.

In the recently published paper of S.S. Medvedev et al. ¹⁶³ the conclusions of a considerable interest have been deduced concerning a protection effect mechanism of benzene rings in radiolysis of polystyrene. Polystyrene is known to have a high radiation stability: in the case of polyethylene formation of a single cross-link requires 25 - 35 e.v., while in the case of polystyrene 3000 - 5000 e.v. are necessary. Basing on investigations of radiolysis of toluene^o labelled by deuterium the authors have concluded that the high radiation stability of polystyrene is largely caused by disproportionation reaction of primary radicals with cyclohexadienyl

^o At the radiolysis of toluene the radicals formed have a structure similar to that of the radicals arising in polystyrene under irradiation.

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type radicals arising in the polymer under irradiation:



Vu.S.Lazurkin and G.P. Ushakov¹⁶⁴ have examined the radiation cross-linking of polydimethylsiloxane. The vulcanizates resulting demonstrate more high strength and resistance to freezing than that obtained by conventional methods. Radiation chemical cross-linking (vulcanization) of resins is an object of research of A.S. Kuminov, ~~V.L. Karpov~~ V.L. Karpov and T.S. Nikitina^{165, 166}. Radiation vulcanization of different resins has been established by the authors to can be a method of preparation of rubbers with new valuable properties.

S.A. Pavlova, S.R. Rafikov, B.L. Fostlin¹⁶⁷ have obtained experimental evidence that the two opposite reactions, i.e. reaction of cross-linking and that of destruction under action of radiation on polyamides proceed simultaneously. [The authors have accomplished combined investigations including the change of mechanical properties, as well as the properties of the solutions, the change of molecular weight and molecular weight distribution function of the irradiated material. By this means they have succeeded in distinguishing of the two parallel reactions of cross-linking and destruction. However, the cross-linking is a predominant process and vulcanization of polyamide is an final result of irradiation of this material.

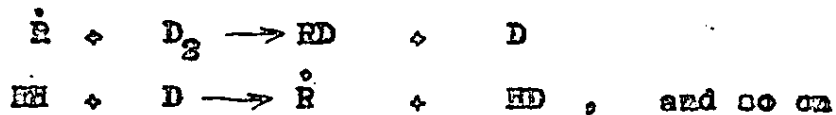
Recent investigations of changes in the properties of

polymer immediately in the course of their irradiation accomplished by soviet scientists are of a considerable interest. Yu.S.Lazurkin et al.¹⁶⁸ have examined the change of mechanical properties of different polymers in the course of irradiation from nuclear reactor. Reversible radiation-mechanical effects have been observed to appear in the course of irradiation, i.e. change of mechanical properties appears in the time of irradiation and disappears after irradiation has been stopped. Reversible changes in gas-penetrability of polymers in the time of γ -irradiation have been examined by V.L.Karpev et al.¹⁶⁹. It has been found that when the Co^{60} source of γ -radiation is put in or out the rate of gas diffusion through the polymer undergoes a sharp change, approaching after irradiation the original value, but still remaining slightly higher than the latter.

Ya.M.Varchavsky, O.Ya.Vasiliev, V.L.Karpev, Yu.S.Lazurkin and I.Ya.Potrov¹⁷⁰ have studied isotope exchange between deuterium gas and different solid polymers in radiation field of a nuclear reactor to examine whether hydrogen from gaseous phase can be implanted into polymer molecules in course of irradiation. Polyethylene and polycyclopentadiene have been proved to trap the most amount of hydrogen in comparison with other polymers examined. The rate of isotope exchange is more slow in the case of polybutadiene and polystyrene. The authors have suggested that the intrusion of deuterium is caused by recombination of polymer radicals arising under irradiation and

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Counterion molecules:

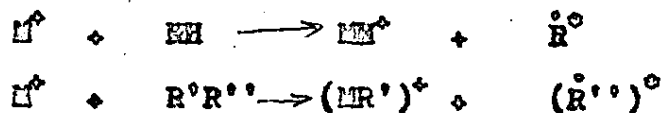


Use of isotope exchange technique in wide scale will, undoubtedly, assist to understand more completely the mechanism of polymer radiolysis.

7. Radiation elementary acts and primary chemical processes

In all chemical transformations in irradiated material secondary electrons, ions, excited molecules and free radicals (including atoms) are involved. The identification of these products is of a significant importance for elucidation of mechanism of radiation-chemical reactions. This problem is solved by means of mass spectrometry, electron spin resonance, etc.

V.L.Tol'poco and E.L.Frankovich¹⁷¹ employing mass spectrometry technique to investigation of products formed under electron impacts in some simple inorganic and organic compounds in gaseous phase, have found that the ion-molecule reactions playing an important part in primary radiation-chemical processes can give excited radicals:

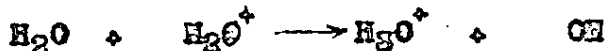
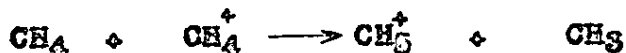


This phenomena has been observed in many processes in vapour phase [including $H_2^+ + H_2O \rightarrow H_3O^+ + H$; $CH_4^+ + H_2O \rightarrow H_3O^+ + CH_3$; $C_3H_9^+ + H_2O \rightarrow H_3O^+ + C_3H_7$, etc.]

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In another paper V.L.Tal'poco¹⁷² has pointed out that formation of different type traps under irradiation (especially in the case of hydrocarbons) can play an important part in radiation chemistry. Under irradiation of saturated hydrocarbons can arise unsaturated compounds and free radicals ionization potentials of which are lower than those of molecules of original substance. Such compounds and radicals can act as p- and n-traps. Increasing of amount of the traps in condensed phase creates the conditions which favour the principal elementary processes consisting in recombination of "plus-minus" pair to be influenced with an adjacent free valence. One of two radicals arising at the recombination can add to this free valence, the probability of the latter process being, practically, equal to the unit in the case of hydrocarbon system.

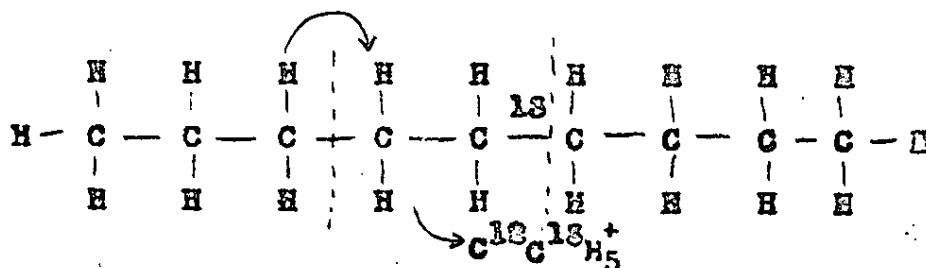
[Of great interest is employment of pulsed irradiation for measurement rate constants of ion-molecule reaction. Combining pulsed irradiation and mass spectrometry technique V.L.Tal'poco and E.L.Frankovich¹⁷³ have determined rate constants for the following reactions:



At 570° K the rate constant of the former is equal to $11.6 \cdot 10^{-11}$ cm³/mol.sec., that of the latter is $9.5 \cdot 10^{-10}$ cm³/mol.sec. at 410° K.

N.N.Tunichy et al.¹⁷⁴⁻¹⁷⁵ are studying dissociation of rather large molecules under electron impacts using mass

spectrometry technique. Examination of mass spectra of halogenated hydrocarbons ¹⁷⁴⁻¹⁷⁵ indicated that with increasing of halogene atom quantity in the molecule the per cent of molecular ions in mass spectra decreases. The authors have also found ^{176,177} that the most complete agreement of calculated and experimental data take place when approximately equal probability of fragment ion formation from every part of molecule is supposed. For instance, in mass spectrum of n-nonane-¹³C ions $C^{13}H_9^+$, $C^{12}C^{13}H_8^+$ and $C_2^{12}C^{13}H_7^+$ have been observed in amounts which are approximately equal to value which can be calculated proceeding from the assumption mentioned above. Based on analysis of mass spectra the authors have proposed the following scheme of large molecules disassociation:



Quite recently V.L.Tal'rose and E.L.Frankevich ¹⁷⁹ have carried out a comparative investigation of induced electrical conductivity and behaviour of free radical in irradiated solid paraffin. They have measured conductivity of paraffin irradiated at 77° K in the time of "annealing". In this case a sort of "flaring-up" of conductivity have been discovered (Fig. 10). This phenomenon appears as follows. At temperature differing by some dozens degree from the temperature region "dark" conductivity take place, a considerable magnitude of conductivity is observed. A further increasing of temperature

10.
concentration of radicals
2 - relative variation
of the conductivity
after line - variation
of the dark conductivity

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ture the conductivity reduces to "dark" conductivity. The time-temperature ^{region} of "flaring-up" is coincident with the region where decreasing of ESR-signal is observed. Based on these data the conclusion has been deduced ^{according} to which formation of ions in irradiated solid or liquid material can proceed through formation of free radicals.

Fig. 10

V.V. Vozvedsky et al 162, 180-185 are carrying out investigation of radicals appearing in radiolysis of organic and inorganic systems using electron spin resonance techniques.

[The apparatus permitting the observation of ESR-spectra in the course of irradiation with fast electrons has been constructed by the authors 162, 180. By means of this apparatus ESR spectra and radical formation kinetics have been studied. The radicals forming under irradiation of teflon in vacuum at low temperature have been found to have a long life-time. In the air they convert peroxide radicals $-CF_2 - O - CF_2 -$ which can be stored at room temperature for some 0 - 0.5 months.

[In the case of benzene radicals C_6H_5 and C_6H_7 have been found to form 182,



In polyphenyls (diphenyl, p-ditolyl, etc) abstraction of H-atoms and CH_3 - groups situated in para-position with respect to phenyl substituent occurs to form a radical being analogous to C_6H_7 .

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✓ In this review we have not discussed some other branches of radiation chemistry developing in the USSR. This paper, for instance, does not contain any description of effects of ionizing radiation on catalysts and semi-conductors, neither does it contain chemical kinetics or design of radiation sources. Nevertheless, the contents of the review gives an idea of the wide-scale work in the field of radiation chemistry carried out in the USSR.

There is no doubt that in the next years and decades more and more power radiation sources than at present will be available. Elementary particle acceleration technique is going to be improved day by day. Power of nuclear reactors is also growing. It becomes then possible to obtain more and more highly active preparations of artificial radioactive isotopes. Energy released by uranium nucleus fission^{can}, undoubtedly, be used in future for new chemical processes to be put in practice. All these open bright perspective for radiation chemistry, which is one of the most progressive branches of modern physical chemistry and special chemical engineering.

Exchange of scientific successes achieved in this important field between scientists of different countries will promote the further progress of chemical science and its applications in interests of whole mankind.

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Captain to Flight

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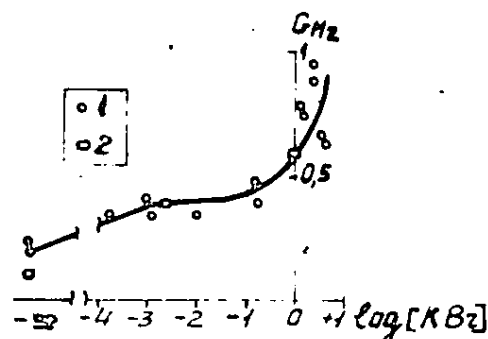


Fig.1. The dependence of $G(H_2)$ on molar concentration of KBr solution under the action of protons with energy 660 Mev (1) and γ -radiation of Co^{60} (2)

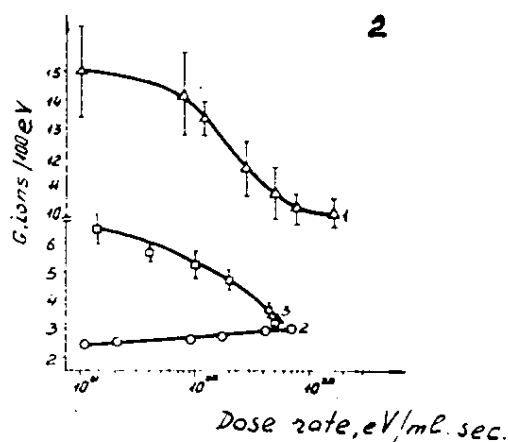


Fig.2. The effect of high dose rates of radiation upon the yields of radiolytic transformations in aqueous 0.8 N sulfuric acid solutions:

- 1 - the dependence of $G(Fe^{++})$ on dose rate in $3 \cdot 10^{-3} N$ solution of ferrous ammonium sulfate;
- 2 - the dependence of $G(Ce^{++})$ on dose rate in $2 \cdot 10^{-4} N$ solution of ceric sulfate;
- 3 - the dependence of $G(Co^{++})$ on dose rate in solution of the mixture of $Ce(SO_4)_2$ and $Tl_2 SO_4$ (concentration is $2 \cdot 10^{-4}$ and $1 \cdot 10^{-2}$ respectively)

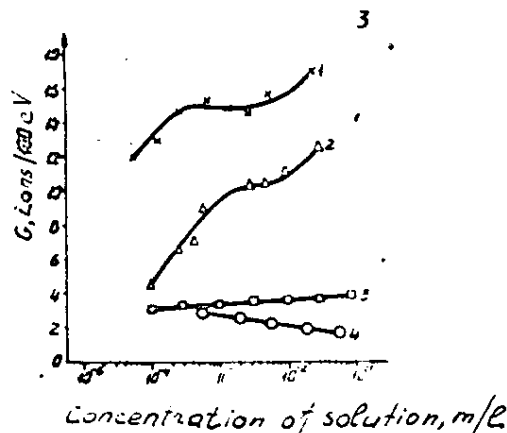


Fig.3. The dependence of the yields of radiolytic transformations on concentration of solution at high dose rates of radiation

1 - the effect of concentration of ferrous ammonium sulfate in aqueous 0.8 N sulfuric acid solution saturated with air on $G(\text{Fe}^{+++})$ at dose rate 10^{21} eV/ml. sec;

2 - the same at dose rate $3,5 \cdot 10^{22}$ eV/ml. sec;

3 - the effect of concentration of thallous sulfate in 0.8 N sulfuric acid solutions of the mixture of Co^{+++} and Tl^+ salts saturated with air on $G(\text{Co}^{+++})$ at dose rate $4,5 \cdot 10^{22}$ eV/ml. sec;

4 - the effect of concentration of cerous sulfate in 0.8 N sulfuric acid solution of the mixture of Co^{+++} and Ce^{+++} salts on $G(\text{Co}^{+++})$ at dose rate about $5 \cdot 10^{22}$ eV/ml. sec.

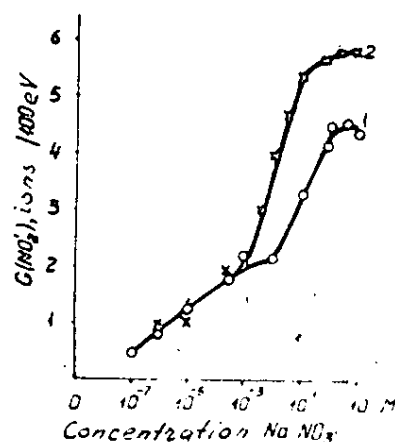


Fig. 4. The dependence of $G(\text{NO}_2^-)$ on concentration of NaNO_2 in solution saturated with nitrogen ($\text{pH} \approx 14$):

- 1 - in absence of glycerol
- 2 - in presence of glycerol at 10^{-3} concentration.

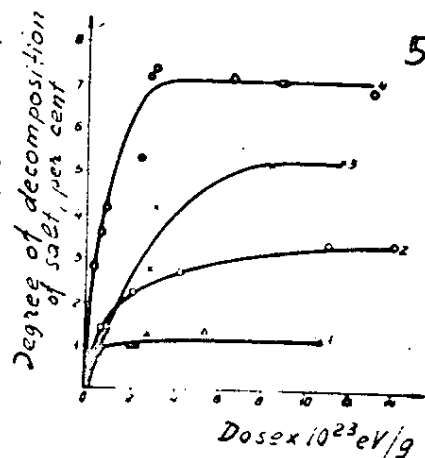


Fig. 5. Decomposition of complex salts of platinum under the action of high energy electron beams depending on integral dose.

- 1 - $(\text{NH}_4)_2[\text{PtCl}_6]$
- 2 - $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$
- 3 - $\text{cis}-[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
- 4 - $\text{trans}-[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

Temperature of the experiments was $145-150^\circ \text{C}$.

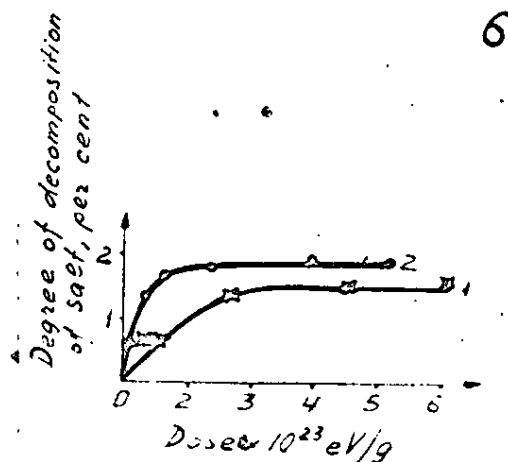


Fig.6. Decomposition of potassium chloroplatinate (1) and ammonium chloroplatinate (2) under the action of high energy electron beams. Temperature of the experiments was 20-25° C.

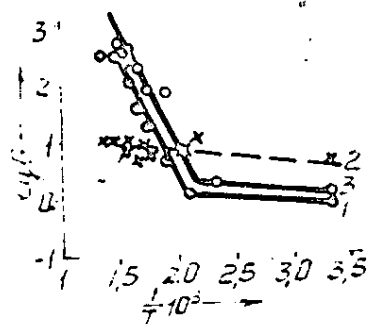


Fig.7. The dependence of logarithm of radiation-chemical yield of methane (1), hydrogen (2) and hydrocarbon fraction C_2-C_3 (3) on inverse temperature of the radiation thermal cracking.

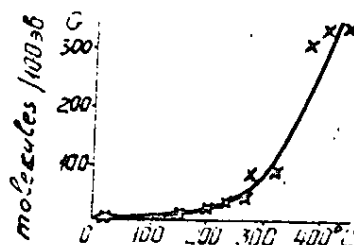


Fig. 8. The dependence of radiation-chemical yield of liquid olefins upon temperature of the radiation thermal cracking.

9.

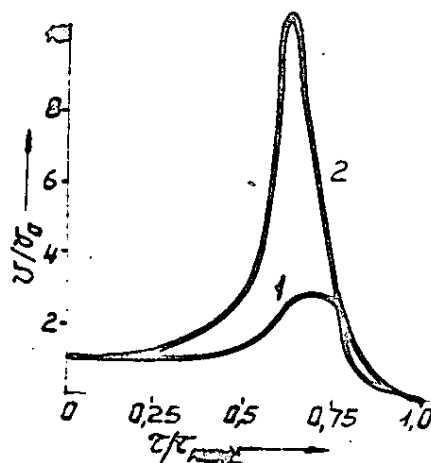


Fig. 9. The influence of a mode of initiation on the shape of the kinetics curves of polymerization of methyl methacrylate (temperature 60° C):

1 - polymerization of pre-irradiated monomer (dose $6 \cdot 10^{20}$ eV/cm^2)

2 - polymerization of methyl methacrylate in presence of benzoyl peroxide (0.01 %).

v/v_0 is the ratio of the polymerization rate in a given moment to the initial rate;

τ/τ_{max} is relative duration of polymerization process.

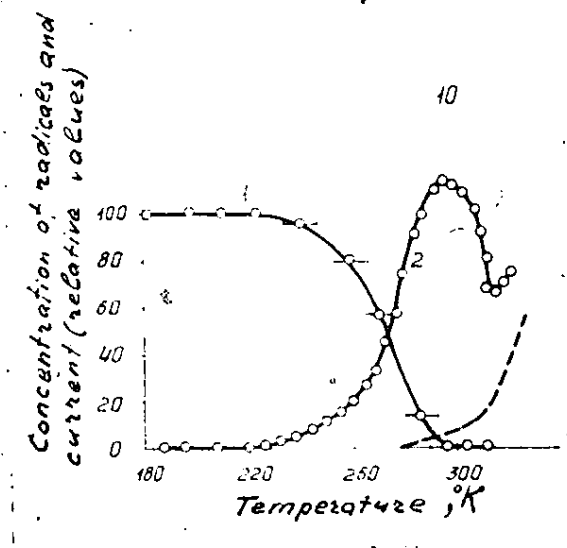


Fig. 10. Variation of radical concentration and electrical conductivity of irradiated paraffin under heating.

Heating rate is equal to 22° C/min.

- 1 - concentration of radicals (in arbitrary units)
- 2 - relative variation of the current through the sample at 1000 volts potential difference between the electrodes placed inside the sample. Variation of the dark conductivity is indicated with the dotted line.

THE DEVELOPMENT OF RADIATION CHEMISTRY

IN THE U.S.S.R.

by
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Introduction

The study of chemical changes of substances brought about by high energy radiation has begun its rapid development in connection with the availability of the power ionizing radiation sources. The development of radiation chemistry was stimulated first of all by requirements of nuclear engineering and problems of the reliable protection against the hazardous radiation. On the other hand, the radiation chemistry deals with the phenomena called forth by high-excited and of high reactivity particles, i.e. ions, free radicals,

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and molecules. The latter is caused by the fact that energy of ionizing radiation is many times as large as the chemical bond energy. The generation of excited particles mentioned is the main distinctive feature of radiation-chemical processes in comparison with the photochemical those where such phenomena do not almost occur. This circumstance has also promoted to the growth of interest in radiation chemistry and its uses in practice.

Russian and soviet scientists made a substantial contribution in the development of radiation chemistry. Thus, among the first investigators having observed chemical effects of ionizing radiation upon diverse compounds there was N.A.Orlov. In 1904-1906 he founded¹ that paraffin, wax, stearic acid and other solid organic substances converted into liquid resinous products. In 1910 N.D.Zelinsky² placed in a sealed tube some little crystals of radium bromide containing 0.5 mg of pure radium and 1.5 ml of cyclohexene (C_6H_{10}). The investigation carried out after several years revealed the deposition of free carbon on surface of the bromide crystals, the liquid decomposition products being consisted not only of hydrocarbons more simple than cyclohexene but, also, of more heavy hydrocarbons synthesized under action of alpha particles emitted by radium. As an intermediate process, apparently, dehydrogenation of the original material occurred.

N.D.Zelinsky stated that relative processes could take place in the nature under effects of radiation of radium contained in rocks.

[Modern] development of radiation chemistry in this country has begun in the post-war years, being caused by uses of nuclear power for various purposes. This period is characterized by rapid development of wide-scale research work embracing more and more diverse classes of compounds and reaction types and, on the other hand, by employment of modern research techniques involving gas-liquid chromatography, electron paramagnetic resonance, mass spectrometry and so on for identification of radiolysis products and for elucidation of the reaction mechanism. As ionizing radiation sources nuclear reactors, spent heat releasing elements of atomic power reactors, γ -ray sources of Co^{60} and Cs^{137} , α -emitters such as radon and polonium preperates, betatrons (including these with extracted electron beams), electron accelerators permitting both continuous and pulsed irradiation, X-ray installations and so on are employed.

These are radiation-chemical research laboratories in various regions of the USSR. A number of the Moscow research institutes are carrying out investigations in this field. Radiation-chemical investigations are accomplished in the Ukrainian SSR, Georgian SSR, Uzbek SSR and other republics having atomic reactors. The fact that in recent three years about three hundred publications on this topic have been issued by soviet investigators illustrates the development of the radiation chemistry in this country. In 1957 the first All-Union conference on the radiation chemistry was held in Moscow, where 56 papers were reported and discussed ³.

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A large number of the soviet investigations in this field was reported on the other scientific congresses and conferences in this country as well as abroad 4-10.

[Authors of this paper] shall, in the main, describe the most important directions of research in the radiation chemistry in the USSR and also shall review some interesting papers published in 1958-1960. [The previous soviet works are published in form of separate collections 11-12, transactions of a number of conferences 4-7, and are also told in reviews 13-16 and booklets 17-18 edited in the USSR.

2. Radiation chemistry of water and aqueous solutions

The radiation-chemical reactions occurring in water and aqueous solutions were an object of many investigations having been carried out during the last years in this country. This is caused first of all by the fact that water is used as a moderator and a coolant in atomic reactors; besides, in aqueous solutions many processes take place involved in the nuclear fuel production and isolation of nuclear reaction products. Moreover, behaviour of aqueous solutions under irradiation is analogous, in a considerable extent, to that of biological systems. That is why the study of the effects of ionizing radiation up on the aqueous solutions can be assumed as basis for estimation the effects of radiation on living tissue.

Soviet research works cover a wide range of diverse questions of the radiation chemistry of water and aqueous solutions. The influence of a ionization density and dose

rate on the yields of radiolytic conversion in the aqueous solutions, the role of direct action of radiation on dissolved substance, the role of excited molecules of water in radiolysis processes, dependence of the yields of molecular products of radiolysis on concentration of solution were ascertained. Radiation-electrochemical processes and the influence of irradiation on corrosion behaviour of metals and some other questions were an object of a number of investigations.

At present is generally accepted that under the action of radiation on water atoms H and radical OH, as well as molecular hydrogen and hydrogen peroxide are generated as primary products of the radiolysis. These intermediate products interact further with the dissolved compound. In the case of the diluted aqueous solutions it is possible in this way to explain the character and the yield of the radiolysis products and, in some cases, the radiolysis kinetics also. Based on this conception systematic investigations are carried out in the USSR. [V.Yu.Filinovsky and Yu.A.Chizmadzhev¹⁹ have made calculations concerning the dependence of the molecular products yield in the case of the radiolysis of water under the action of radiations with high ionization densities in the presence of scavengers. Two cases of atoms H and radicals OH distribution during water radiolysis have been considered: 1) both radicals are in a track column with the diameter ~ 8 and 2) atoms H have more diffusive distribution ($\sim 100 \text{ \AA}$).]

B.V.Frahler et al.²⁰ have compared the rate of radiation-chemical decomposition of hydrogen peroxide with the

most reliable data available in the world literature concerning the radiolysis of water under the action of γ -radiation of cobalt-60. The authors have confirmed the applicability of hypothesis about the constancy of yields of radiolysis products of water as well as the adequacy of the law of homogeneous kinetics to the case of radiation chemical processes in diluted aqueous solutions.

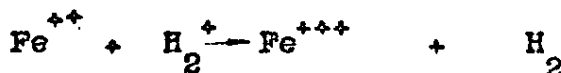
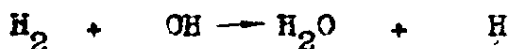
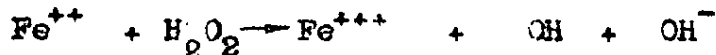
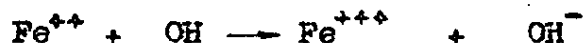
In an other paper B.V. Ershler²¹ basing on the model of irradiated solution in which free radicals and molecular products are distributed homogeneously in the total irradiated volume, has considered general regularities of the radiolysis, for the cases wherein this model is applicable. Proceeding from the assumption that radiolysis products yields of water are constant values and that in the solution only bimolecular reactions proceed, the author has considered the effects of radiation intensity on the dependence of yield upon concentration. Two criteria for the adequacy of this model have been found. In the case of stationary state, the increase of intensity from I_1 to I_2 displaces the curve representing the dependence of a logarithm of concentration of one of radiolysis products upon a logarithm of concentration of other product, along the coordinate axes by a segment which is equal to $\Delta I^{\frac{1}{2}}$, the shape of the curve being unchanged. If stationary state is not yet achieved, the variation of intensity leads to displacement by the same value $\Delta I^{\frac{1}{2}}$ along the abscissa of the curve representing the dependence of the radiation yield G of one product with logarithm of concentra-

tion of another. Radiolysis of the solutions of hydrogen peroxide²⁰ is an example of such a regularity.

It is known that increase of concentration can bring the conditions in which the dissolved compound would interact not only with free radical distributed in whole volume of solution but also with those in the points of high ionization density, competing thus with recombination reaction of radicals and reducing the molecular product yield. In this connection the investigations of P.I.Dolin with collabor., N.A.Bakh with collabor., M.A.Proskurnin with collabor., are of considerable interest. Examining the nitrate systems²²⁻²⁴, as well as the aqueous solutions of potassium bromide²⁵⁻²⁶, it has been found that a substantial part of molecular hydrogen originates from the recombination of atoms H. For instance, decreasing of magnitude of $G(H_2)$ till some hundredths of molecules per 100 electron-volt with the increasing NO_3^- -ions concentration has been found²²⁻²⁴.

From the point of view of elucidating the mechanism of radiolysis oxidation of Fe^{++} -ions in diluted aqueous solutions of considerable interest is the work of V.N.Shubin and P.I.Dolin²⁷, in which the effects of a pressure of hydrogen above the solution on the yield $G(Fe^{++})$ is investigated. It was found that variation of the pressure of hydrogen in the range from 1 to 180 atm. does not exert an appreciable influence on system concerned. [A mechanism has been suggested for this case which includes the following reactions:

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The results obtained confirm the hypothesis according to which in deaerated solutions atoms H take part in oxidation of ions Fe^{++} , directly or by means of formation of the ions H_2^+ .

It is known the yields of radical and molecular products of water radiolysis are dependent on the magnitude of linear energy transfer, i.e. on kind of radiation. Although a number of soviet investigations hitherto carried out in this topic is not large, they are of a certain interest. A.M. Kabakchi et al.^{28,29} has investigated effects of γ -radiation of cobalt-60, β -rays of phosphorus-32 and α -particles of plutonium-239 on aqueous solutions of nitrates in various concentration. Radiation-chemical yield of NO_2^- , according to the authors mentioned is dependent on the kind of the radiation. For instance, under the action of α -radiation of Pu^{239} $\text{G}(\text{NO}_2^-)$ is considerably less, than that in the cases of γ -rays of Co^{60} and β -particles of P^{32} .

Z.V. Efshova and M.V. Vladimirova³⁰ have studied the action of alpha-particles of polonium on 0.8N aqueous solutions of H_2SO_4 . It has been found that the initial yield of hydrogen peroxide (1.2 molecules per 100 ev) is independent on

-3-

concentration of polonium dissolved in the range of specific activity from 0.1 to 12 millicuri per ml, concentration of H_2O_2 tending to its limit value. For 0.8 N H_2SO_4 the equilibrium limiting value of the H_2O_2 concentration amounts $5-9 \cdot 10^{18}$ molecules per ml.

8.A.Brucentsova and P.I.Dolin⁵¹ have investigated the action of protons with the energy 660 Mev on aqueous KBr solutions. The linear energy transfer of the radiation mentioned is nearly to that of 1 Mev electrons. The work has demonstrated that the radiation-chemical phenomena are defined solely by the magnitude of the linear energy transfer. Thus the yields $G(Fe^{+++})$ obtained in the case of aqueous ferrous sulphate solution and $G(H_2)$ obtained for KBr solutions of various concentration (Fig. 1) have been found by the mentioned authors to be approximately equal to the corresponding values obtained under action of γ -radiation of Co^{60} .

Fig. 1.

A.K.Pikaev and P.Ya.Glazunov³²⁻³⁷ have studied radiolytic transformations in aqueous solutions of several inorganic compounds at high dose rates. The latter have been achieved by means of pulsed electron radiation; the electron energy has been 0.8 - 1.0 Mev; the pulse duration - 5 μ sec. The radiolytic conversions in aqueous solutions of ferrous sulphate and ceric sulphate, of the mixtures of Co^{+++} and Tl^+ sulfates and also Co^{+++} and Co^{++} sulphates have been investigated. The Fig. 2 indicates the dependence of $G(Fe^{+++})$, $G(Co^{+++})$ in the absence of Tl^+ and also $G(Co^{+++})$ in the

1- action of protons
2- action of γ -rays
3- action of Co^{60}

-10-

presence of Tl^+ upon dose rate, obtained by the authors. As one can see from the Fig. 2, the appreciable variation of yields takes place at the high dose rates up from about 10^{21} ev/ml. sec. For instance, $G(Fe^{+++})$ decreases with increase of the dose rate, whereas $G(Ce^{+++})$ under the same conditions increases. This is caused by the fact that at the dose rates up from $\sim 10^{21}$ ev/ml. sec. and higher the processes originated by overlapping of ionizing particle tracks begin to play a significant part, changing the yields of radiolysis products of water $G(H)$, $G(OH)$, $G(H_2)$ and $G(H_2O_2)$.

Fig. 2.

In the papers mentioned above³²⁻³⁷ it has also been observed that at high dose rates the importance of competition between radical-radical and radical-solute reactions is augmented. The Fig. 3 shows the dependence of the yields of radiolytic conversion in several systems upon the concentration of dissolved substance at high dose rates of radiation, found in above mentioned works.

Fig. 3.

The mechanism of radiolytic transformations in concentrated solutions is a problem of to-day. In this case not only the effects of radiation caused by the action of water radiolysis products on the dissolved substance take place, but also direct action of radiation on it is involved. A. L. Kabakchi is one of the first investigators having proposed the conception of the direct action³⁸. He has shown that in the radiolysis of aqueous chloride solution molecular

-11-

chlorine is formed, the yield of which increases in proportion to increasing solute concentration independently of the kind of radiation or the cation nature.

A different point of view has been suggested by M.A. Preskurnin et al.^{14,23,24,39-43}. According to their hypothesis the high concentration gives possibility to radicals originated not only from ionized molecules of water, but also from excited molecules to be involved in the radiation-chemical reactions. In Fig. 4 the dependence found by the authors mentioned above²⁴ is shown, between the yield $G(\text{NO}_2^-)$ and concentration of NaNO_3 solution. The radiation yield $G(\text{NO}_2^-)$ increases with augmentation of NaNO_3 concentration reaching a constant value in the region $5 \cdot 10^{-4}$ - 10^{-2} M. The authors have suggested that existence of this slightly sloping segment of the curve can be explained by involving of practically all the H-atoms formed in the reaction with nitrate-ions. In the more concentrated solutions the yield $G(\text{NO}_2^-)$ increases again, and for the 1-6 M solutions remains constant. According to the authors²⁴ the increase of the yield $G(\text{NO}_2^-)$ in the concentrated solutions is caused by involvement in the process of the H-atoms originated from both the ionized and excited molecules of water.

Fig. 4.

It is M.A. Preskurnin who has discovered the radiation sensibilization phenomena described below. If in a solution one adds a substance capable to interact easily with one of the radical radiolysis products of water, there are

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created conditions in which another radicals are more completely involved in radiolytic conversion. In the case of nitrate system according to ^{14,39,44} such substances are glycerol and glucose. Being active acceptors of OH-radicals these promote $G(NO_2^-)$ to be higher.

The curve 2 in the Fig. 4 represents the dependence of $G(NO_2^-)$ on concentration of $NaNO_3$ solution in the presence of glycerol. Here the yield $G(NO_2^-)$ in the case of highly concentrated solutions reaches a value of ≈ 6 ions/100 ev, what implies involving of all water radiolysis products in the reaction with dissolved substance.

Recently, M.A.Proskurnin et al. ⁴⁵ have proposed the hypothesis according which there are two kinds of excited molecules of water differing in level and type of excitation. This hypothesis can explain the existence of three limiting values of the radiolysis yield of dissolved substance in dependence in various conditions of radiolysis. In the case of nitrate system, as it was mentioned above, the limiting values of $G(NO_2^-)$ are equal to 2, 4, and 6 ions/100 ev.

Radiolytic transformations in concentrated aqueous solution have been investigated by a number of another soviet scientists. The work of L.T.Bugaenko and V.N.Belevsky ⁴⁶ dedicated to the problem of direct action of radiation on the concentrated perchloric acid aqueous solutions is of a certain interest.

As it has been found by A.A.Balandin, V.I.Spitsyn et

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al.⁴⁷, under the effects of irradiation on aqueous solutions of a several complex salts of platinum the presipitation of metallic platinum takes place, product having a higher catalytic ability in the low-temperature reaction of cyclohexene hydrogenation. Palladium black prepared on radiation-chemical method differs, according to the same authors⁴⁸, by its catalytic properties from the material prepared in conventional way.

Radiolytic transformations in aqueous solutions of plutonium have been examined by H.A.Bakh and collab.^{49,50}. Several papers of soviet authors are devoted to radiolysis of aqueous solutions of uranium^{51,52} *and americium*. [V.G.Firesov and B.V. Erahler⁵¹ examining radiation-chemical reactions in aqueous solutions of uranium (IV) have found that under the action of γ -radiation of Co^{60} radicals OH and hydrogen peroxide are responsible for oxidation of U^{+4} -ions. As concentration rises, the oxidation yield at first increases and subsequently is lowered. In the presence of oxygen G (UO_2^{++}) is significantly more (16 eq/100 ev) than that in the degassed solutions. The authors have deduced the equation describing the dependence of G (UO_2^{++}) upon U^{+++} concentration, the ratio of the rate constants of the three reactions ($\text{U}^{+4} + \text{OH}$, $\text{H} + \text{OH}$) and $\text{H} + \text{H}$) being involved.

G.N.Yakovlev with collab.⁵³ examining the effects of inherent α -radiation of Am^{241} on the valency state of americium in the aqueous solution have found that radiation-chemical reduction of AmO_2^{++} ions in a considerable degree

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is dependent on acidity of the solution as well as on nature of the acid. For example, in the concentrated solution of perchloric acid the yield $G(\text{AmO}_2^{++})$ is appreciably lower, than that in diluted solutions. The reduction of NpO_2^{++} ions in aqueous solutions induced by electron radiation⁵⁴ is also dependent on the factors mentioned above. It is of an interest that, from radiation-chemical point of view, the pentavalent neptunium is more stable than other valency states.

Radiation electrochemical processes in aqueous solutions have been an object of several works of soviet authors. N.A.Bakh et al^{22, 55} have examined change of oxidation-reduction potential of several compounds in aqueous solutions under action of ionizing radiation. Extensive investigations of radiation electrochemical processes have been carried out by V.I.Veselovsky and collab.⁵⁶⁻⁶¹. That in the works of the latter it has been discovered that the potential of the platinum electrode in irradiated 0,8 N sulfuric acid solution saturated with nitrogen reaches a value closely approximating to the reversible hydrogen potential and the potential of the gold electrode becomes equal to -0.95 volt.

D.V.Kokoulina, P.I.Dolin and A.N.Frumkin⁶², examining behaviour of smooth platinum electrode in the solution of sulfuric acid in wide range of doses absorbed and dose rates, have been proved that the potential of platinum electrode in irradiated 0.8 N sulfuric acid is controlled by the molecular radiolysis products of water accumulating in solution, i.e. by hydrogen and hydrogen peroxide. The radical products of

-15-

radiolysis in this case do not play any appreciable part in potential establishment on platinum. A similar conclusion has been drawn by S.D.Lovina and T.V.Kalish⁶³ from an examination of the behaviour of nickel electrode under irradiation. [Examining the oxidation-reduction reaction $Fe^{++} \rightarrow Fe^{+++}$ under irradiation P.I.Dolin and V.I.Duzhenkov⁶⁴ have proved the potential possibility of utilization the products of oxidation and reduction in aqueous solutions for the purpose to transform energy of radiation into electrical energy. In other words, the possibility of constructing radiation-galvanic cell has been proved. Another solving of this problem has been stated by V.J.Veselovsky et al.⁵⁹. They have employed the Pt and Au electrodes having selective properties with respect to oxidizing and reducing agents formed in solutions under irradiation.]

There are a number of soviet works examining the influence of ionizing radiation upon the corrosion behaviour of metals in various media. N.D.Tomashov, A.V.Byalobzhesky et al.⁶⁵ have studied the effects of electron radiation on corrosion of iron, stainless steel and aluminium in sodium chloride solutions. A.V.Byalobzhesky^{66, 67} has examined corrosion of metals under irradiation in air. The corrosion of several metals under irradiation (by fast electron beam, γ -rays of Co^{60} , X-rays) has been found by him to be appreciably accelerated by ionizing radiation. The metals examined can be arranged in the following consequence: iron - copper - zinc - aluminium, the corrosion stability increasing. It has been suggested in

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under irradiation is caused by formation of radiolysis products of oxygen, water and nitrogen in the air.

I.L.Rozenfeld and E.K.Oshe^{68,69} have examined the effects of electron radiation on electrochemical activity in various media of zirconium and titanium covered with oxide films having semi-conductor properties. [Diminution of anode and cathode reaction overvoltage and increasing of rate of those reaction have been found. The effect discovered is reversible: stopping of irradiation leads to return of overvoltage and rates of anode and cathode reactions to values closely approximating to original ones. Another phenomenon of an interest discovered by the authors, is the fact that under irradiation behaviour of metals covered with semi-conductor films of p-type and of n-type with respect to anode process is quite different. With respect to cathode reaction such a difference is not observed.]

The corrosion behaviour of several metals under irradiation has also been studied by Ya.M.Kolotyrkin et al.^{41, 70}. For example⁴¹, they have investigated the effects of γ -radiation of Co⁶⁰ on electrochemical properties and corrosion of steel, nickel and platinum in sulfuric acid. It was established, in the case of steel and nickel, that effect of irradiation is equivalent to anode polarization. The authors have confirmed the conclusion by V.J.Veselovsky with collabor.⁵⁶⁻⁶¹ about establishment in sulfuric acid the platinum electrode potential closely approximating a potential of reversible hydrogen electrode.

3. Radiation chemistry of simple inorganic molecules

A number of works by soviet authors is dedicated to study the radiation-chemical reactions of simple inorganic molecules. The attention to these investigations has been attracted, first of all, owing to the fact that the examinations of such reactions allows, more successfully than in cases of other compounds, to correlate the yields and kinetics with ionization and excitation potentials, dissociation energy and other parameters of irradiated material as well as to study the effect of phase state on radiolysis and to correlate radiation-chemical and photochemical processes.

The most complete investigation in this topic accomplished by soviet chemists is radiation chemical oxidation of nitrogen with the oxygen. S.Ya.Pzhezhetzsky and M.T.Dmitriev^{71,72} have examined kinetics and mechanism of oxidation of nitrogen under the action of electron impact. [Nitrogen pressure has been varied from 10^{-2} to 10^{-3} mm Hg, electron energy - from units of electron-volts to 200 Kev.] Formation of N_2^+ -ions appears to be an intermediate stage of the reaction. Kinetics of the reaction is described by an equation of the second order, activation energy being in the range 2-7 kcal/mol. [Later, M.T.Dmitriev and S.Ya.Pzhezhetzsky⁷³ have carried out work on oxidation of nitrogen induced by γ -radiation of Co^{60} under pressures up to 150 atm. and at temperatures 15-25° and at 150°C. It has been observed that increasing of pressure from 1 mm Hg to 760 mm Hg lowers the oxidation reaction yield, but at the further increasing of pressure the

yield increases, reaching the magnitude of 5-6 molecules of NO_2 per 100 ev at 150 atm. The yield of N_2O at 3-50 atm at 150°C is 2.5-3.5 mol/100 ev. The dependence of the reaction rate on composition of mixture obeys to an equation of the second order. A deviation from the equation of the second order has been observed for the dependence of reaction rate and yield on the pressure, because of recombination of ions formed under irradiation.

Recently M.T.Dmitriev and S.Ya.Pshezhetsky⁷⁴ have examined the transformation occurring in nitrogen dissolved in water under action of γ -radiation of Co^{60} and a beam of fast electrons. It has been found that nitrogen dissolved in water under irradiation is fixed in form of nitrate, nitrite and ammonia. The yield of the reaction is dependent on a composition of mixture of gas dissolved and its pressure. For instance, the yield of nitrogen fixed is 0.09-0.18 at 1 atm. and 1.0-1.4 atoms at 150 atm. per 100 electronvolts of radiation energy absorbed.

S.Ya.Pshezhetsky et al^{75,76} have also studied the formation of ozone in liquid and gaseous oxygen under action of γ -radiation of Co^{60} and fast electron stream. Excited molecules of oxygen have been proved to play an important role in the reaction. The radiation-chemical yield of O_3 is 12-15 molecules/100 ev in the case of liquid phase and 1.5 molecules/100 ev for the gas.

Hydrazine is formed under the action of fast electron

beam on liquified ammonia ⁷⁷. The latter process is characterized by stationary hydrazine concentration owing to the equilibrium between rates of direct and reverse reactions, the yield being 1.0-1.2 molecules/100 ev.

It has been studied the kinetics of hydrogen peroxide decomposition depending on its concentration in aqueous solution under action of γ -radiation of Co⁶⁰, ultraviolet light as well as the analogous dependence for the rate of the thermal decomposition ⁷⁸. The rate of the reaction as the concentration increases has been found to have always a maximum. It has also been observed that the rate of the radiation-chemical reaction is proportional to square root of radiation intensity. The activation energy of the radiation-chemical reaction is 6.5 kcal/mol, that of the photochemical reaction being 8-9 kcal/mol. The yield of the radiation-chemical reaction is dependent on temperature. Dependence of a degree of electrolytic dissociation of NO₂-radicals on the concentration of the solution is proposed in the paper for explanation of kinetics of the reaction of H₂O₂ decomposition.

Several papers of soviet authors deal with investigation of effects of ionizing radiation on solid substances.

V.I.Spitsyn et al. ⁷⁹ have examined decomposition of solid complex compounds of platinum under the action of electron radiation. In these cases formation of free metallic platinum was sometimes observed. [The magnitudes of the initial yield of metal are represented in the table 1.] The data of the table show that a degree of decomposition of the

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complexes is dependent on nature of the salt and space isomerism. For instance, trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ has lower radiation-chemical stability, than that of the cis-isomer. As it is obvious from the Fig. 5 and Fig. 6, the degree of decomposition of the complex salts remains unchanged at the high integral irradiation doses. In these conditions the process of re-oxidation of free metallic platinum by atomic chlorine brought about with radiation-chemical decomposition of the compounds concerned has apparently a significant part.

Table 1

The initial yields of free metallic platinum
at irradiation of complex compounds

Compound	Initial G (Pt), atom/100 ev.
$\text{K}_2[\text{PtCl}_4]$	0.018
$(\text{NH}_4)_2[\text{PtCl}_4]$	0.143
$(\text{NH}_4)_2[\text{PtCl}_6]$	0.090
$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$	0.047
$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ -cis	0.036
$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ -trans	0.338

M.A. Proskurnin et al. have investigated the effect of γ -radiation of Co^{60} on solid NaNO_3 and KClO_4 as well as on crystalline hydrates of nitrate salts. A paper is of a certain interest describing the effect of dose rate of γ -radiation of Co^{60} in the region of $0.2 \cdot 10^{16}$

Fig. 5.
Fig. 6.

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to $4.1 \cdot 10^{16}$ ev/ml. sec. on the radiolysis product yields of several crystalline hydrates of nitrate salts. It has been proved that a minimum on the curve expressing the dependence of $G(\text{NO}_2^-)$ upon dose rate is a characteristic feature for all crystalline hydrates examined, the position of the minimum being determined by nature of the cation. The crystalline hydrates are more sensible to the action of γ -radiation than the corresponding anhydrous salts.

V.V. Boldyrev et al.⁸⁴ have considered the effect of preliminary irradiation on the rate of thermal decomposition of silver oxalate contaminated with cadmium. The preliminary irradiation with γ -rays of Co^{60} brings about an intensive acceleration of the subsequent thermal decomposition of pure silver oxalate. Thermal decomposition of the salt containing traces of cadmium is accelerated, too, but in a considerably smaller degree. On an opinion of the authors the phenomenon is caused by the formation in the presence of cadmium in crystal lattice additional number of cation vacancies, which can trap positive holes or argentum cations from interstitials.

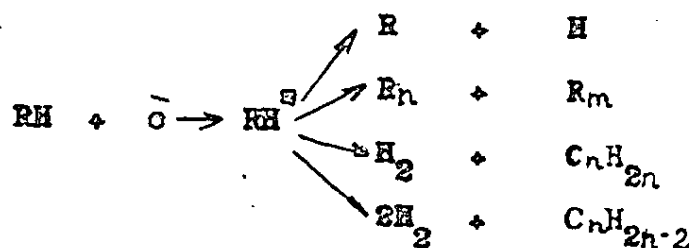
4. Radiation chemistry of organic compounds

The reactions of organic compounds induced by ionizing radiation are objects of research work of a number of soviet investigators. The works are carrying on in several directions.

A.V. Topchiev and L.S. Polak with collaborators⁸⁵⁻⁹² are carrying out the systematic investigation of the effects of

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γ -radiation of Co^{60} and of fast electron beam on hydrocarbons in gaseous, liquid and solid phases. Based on experimental data the following possible types of initial radiolysis reaction of normal alkanes have been suggested in their papers.



Examination of ESR-spectra of irradiated at 77°K in frozen state n-heptane indicated the occurrence of free alkyl radicals and also of H-atoms but in a smaller number. It has been proved that those radicals can be kept at low temperature over a long period of time.

It has been found by the authors mentioned above as well as by foreign authors that the total yield of the radiolysis products of hydrocarbons at room temperature is about 10 molecules/100 e.v., the predominant process being dehydrogenation. The examination of the radiolysis of n-heptane is the most detailed. At irradiation of n-heptane in ordinary conditions the gaseous radiolysis products contain about 80 % of hydrogen. The rest of 20 % includes saturated and unsaturated hydrocarbons.

In the series of soviet investigations in radiation chemistry of hydrocarbons those of radiation thermal cracking of hydrocarbons are of a significant interest⁹⁰⁻⁹². It has been found that at simultaneous action of radiation and

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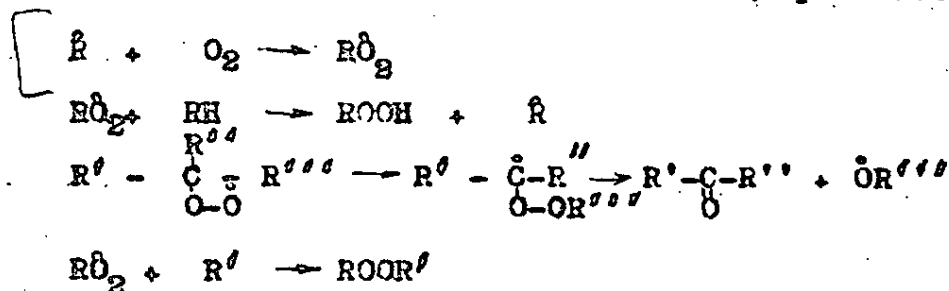
heat the chain reaction of cracking occurs, initiation of the reaction being caused by radiation, while propagation of the reaction being maintained on account of heat energy. For instance, as one can see in Fig. 7, irradiation of n-heptane at elevated temperatures leads to the sharp increasing of yields of hydrocarbon products of radiolysis. Moreover, among the products of radiolysis an increase in unsaturated hydrocarbons content is noted (Fig. 8). One can suppose that the radiation thermal cracking of hydrocarbons should be a perspective method as regards to uses of nuclear radiation in the practice purposes.

Fig. 7.

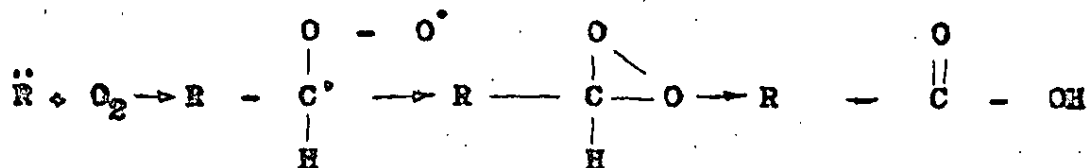
Fig. 8.

Another branch of radiation chemistry of organic compounds developed by the soviet scientists is study of radiation induced oxidation processes in organic systems. N.A. Bakh with collabor. ⁹³⁻⁹⁴ [are carrying on the most methodical research in this topic, under utilization of diverse types of radiation: X-rays, γ -radiation of Co^{60} , fast electrons, mixed radiation of a nuclear reactor. Authors mentioned above] ⁹⁵ are first to have found ⁹³⁻⁹⁴ that under irradiation of liquid hydrocarbons (heptane, isooctane, benzene, cyclohexane, etc.) saturated with oxygen the oxidation of the hydrocarbons at room temperature occurs generating peroxides, carbonyl compounds, alcohols, acids, etc., the formation these compounds being simultaneous right from start of irradiation. In the case of hydrocarbons in ordinary conditions the reaction of oxidation is not chain reaction. Ethyl alcohol and acetone, molecules of which contain more movable atoms of hydrogen are oxidized on the chain mechanism with short chain. The

following scheme suggested by N.A.Bakh, for explanation of radiation induced oxidation is based on the supposition that peroxide radicals can be formed by addition of oxygen molecules to the free hydrocarbon radicals. The simultaneous formation of the radiolysis products is caused by occurrence of some parallel reactions of the peroxide radicals of one type or by simultaneous formation of the various peroxide radicals:



Biradical \dot{R} , which can also arise under irradiation of hydrocarbon, interacting with oxygen gives a molecule of acid:



Oxidation of methane by oxygen at room temperature under action of fast electron beam has furthermore been studied by B.M.Mikhailov et al. ¹⁰⁰⁻¹⁰². They have not observed any chain reaction of oxidation, too.

N.A.Bakh as well as M.I.Proskurnin are carrying out investigations of radiation induced oxidation of organic compounds in aqueous solutions. In this case oxidation is mainly caused by interaction of radiolysis products of solvent with dissolved substances. Hence the oxidation can here take place even in absence of molecular oxygen.

✓
H.A. Proskurnin et al.¹⁰³⁻¹⁰⁴ have conducted a detailed examination of radiation chemical oxidation of benzene into phenol in aqueous solution. They have observed an interesting phenomenon: the yield of phenol in presence of Fe^{++} -ions can increase 3 times as against the ordinary yield and amounts 6 molecules/100 ev. It has been also examined radiation induced oxidation of chlorobenzene in aqueous solutions¹⁰⁵. It has been proved hydrolysis of chlorobenzene plays an important part in the radiolysis.

H.A. Bakh et al.¹⁰⁶ have investigated oxidation of ethyl and isopropyl ether in aqueous solutions under action of X-rays and fast electron beam. In the presence of oxygen the process of their oxidation proceed by chain mechanism. Products of the reaction in both two cases are peroxides (the yield is about 80 molecules/100 e.v.), carbonyl compounds (the yield is about 25 molecules/100 e.v.), alcohols and acids.

At high temperatures, as it has been shown by N.M. Emanuel¹⁰⁷ and H.A. Proskurnin et al.^{108,109}, chain oxidation of hydrocarbons under action of radiation takes place. For instance, it has been observed that under action of γ -radiation paraffin in the presence of oxygen is effectively oxidized at 127-130° C giving fatty acids. The process of oxidation proceed by the degenerated chain-branching mechanism.

Recently V.A. Bakh and Tung Tyan'-chzhen'¹¹⁰ have examined the temperature dependence of radiation-chemical oxidation of n-heptane and n-octane. For both hydrocarbons studied there are two regions of temperature dependence of the yield

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of oxidation products. At the temperature below 70°C small yields and independence on temperature are observed. At temperature above 70° the yield of radiolysis products sharply increases with temperature, reaching in the case of peroxides the value of 30-40 molecules/100 e.v. In the case of radiation induced oxidation of n-alkanes as it has been shown in the paper mentioned, interference of chain and ordinary reaction mechanism is a distinctive feature. The temperature, at which the chain reaction are initiated, is dependent on nature of irradiated compound.

A number of soviet scientists are studying the effects of ionizing radiation on mixture of organic compounds. The work of Kh.S. Bagdasarian with collabor. ¹¹¹⁻¹¹³ is of a considerable theoretical interest. Examining γ -radiation induced decomposition of benzoyl peroxides in various solvents the authors mentioned above have found that in benzene solutions effective transfer of excitation energy from benzene molecules to peroxide molecules occurs, increasing in a significant degree the radiation chemical yield of its decay.

[For reaction studied excitation energy transfer is observed if molecules of both the constituents of the solution have aromatic groups. For example, in cyclohexane and ethyl acetate solutions the energy transfer from solvent does not occur, and a chain reaction of decomposition of peroxide is induced by radicals formed under irradiation of solvents. However any simple correlation between structure of molecules and its ability to accept the excitation energy does

not exist ¹¹³. For example, azobenzene does not accept the excitation energy, although its molecules contain two phenyl rings conjugated with double bond. Some compounds being active acceptors of the energy are negligibly capable or incapable at all to use the energy for chemical transformation. For instance, such a compound is phenylazotriphenyl methane, which does not dissociate on radicals, under action of excitation energy accepted in spite of the fact that this reaction occurs easily under the action of heat.

In the recent paper of Kh.S. Bagdasarian et al. ¹¹⁴ examination of radiolysis of diluted benzene solutions of organic disulphides containing aromatic and aliphatic substituents has been described. Due to the radiolysis energy transfer from the solvent to the dissolved compound, the yields of decomposition of disulphides have been found to be sufficiently more high than the yield being expected in the case when all amount of energy absorbed by them would be spent completely for their decomposition. The energy transfer efficiency has been found in the work referred to be dependent on the nature of the disulphide. Thus, diphenyldisulphide and dibenzoyldisulphide are approximately identical energy acceptors, while accepting capacity of dibenzoyldisulphide is half of that of the former. Aliphatic disulphides (diethyldisulphide, diacetyldisulphide) manifest more low decomposition yields than those of aromatic disulphides, due to the considerably smaller intermolecular energy transfer efficiency.

A number of papers have been published by soviet authors, dealing with radiation-chemical halogenation, oxidation, etc. P.V.Zimakov et al.¹¹⁵ have examined effects of γ -radiation of Co^{60} on chlorination reaction of benzene in the temperature region from -80 to $+40^\circ \text{C}$. The radiation chemical chlorination of benzene has been found to proceed with the yield of 400000 molecules/100 e.v., the resulting material having elevated content of high-toxic γ -isomer of hexachlorocyclohexane in comparison with industrial product obtained by photochemical method.

The effects of ionizing radiation on mixtures of benzene - ammonia, benzene-carbon tetrachloride, and benzene-carbon tetrachloride with compounds containing fluorine have been examined by A.M.Zimin with collabor.¹¹⁶⁻¹¹⁸. In the mixture of benzene and ammonia under γ -irradiation aniline with a small yield is formed. In the case of the benzene-carbon tetrachloride system formation of monochlorobenzotrichloride has been observed (parallel with some other radiolysis products). In the mixtures of CCl_4 with inorganic fluorides and of benzene with simplest fluorocarbons fluorination of CCl_4 and of benzene takes place.

P.V.Dzhagatsepanian et al.¹¹⁹ have studied chlorination of silicon-organic monomers and polymers under effects of γ -radiation. In another paper of the authors mentioned radiation chemical sulphochlorination and sulphoxidation of paraffins as well as some polymers are described. 120

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Researches on working up of radiation-chemical methods of organic synthesis are carrying out in this country.

K.A.Kochoshkov et al.¹²¹ have proposed the radiation-chemical method of preparation of tin-organic compounds. V.I. Spitsyn et al.¹²² have worked out radiation chemical synthesis of butyl ether of phosphonitryl chloride. The reaction proceeds with a good yield under action of fast electron beam on solution of phosphonitryl chloride in n-butyl alcohol.

Radiation-chemical transformations in dyes and substances of biochemical interest are also being studied by soviet chemists. I.V.Vorochinsky¹²³ has examined the synthesis and transformations of leuco-compounds of the dyes under action of γ -radiation of Co^{60} as well as the effects of γ -radiation on synthesis of indophenol¹²⁴. In a number of soviet papers¹²⁵⁻¹²⁸ the radiolysis of methylene blue in aqueous solution is described. M.A.Prochurnin et al.¹²⁹ examined radiolytic decoloration of indigo carmine solutions. A large number of investigations deals with the effects of ionizing radiation on substances of biological interest, i.e. proteins¹³⁰, aminoacids¹³¹, carbohydrates¹³², animal fats¹³³, etc. Radiolysis of protoporphyrin has been examined by I.V.Vorochinsky¹³⁴.

5. Radiation polymerization

Radiation polymerization, at present, ranks rather high among the problems to be solved for the uses of ionizing radiation in the practice. This is called forth by the fact

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that in the majority of cases the radiation induced polymerization as it has been shown in a number of papers including some papers of soviet authors¹³⁵, proceeds by a chain mechanism, the process being initiated by free radicals arising under irradiation of the monomer.

Researches in radiation polymerization are carried out in many countries. In the USSR the work in this field realize S.S. Medvedev^{135, 136}, Kh. S. Bagdasarian^{137, 138}, A.D. Abkin¹³⁹⁻¹⁴¹, B.L. Tsotlin¹⁴² and other soviet investigators.

Among the recent investigations on this topic that of B.L. Tsotlin, V.A. Sergeev, S.R. Rafikov, V.V. Korshak, P.Ya. Glasunov and L.D. Babic¹⁴², concerning radiation chemical polymerization of methyl-methacrylate, is of a considerable theoretical and practical interest. In the presence of air the methyl methacrylate has been found not to be polymerized under action of ionizing radiation. However, spontaneous polymerization of the irradiated material proceeds at room and lower temperature to the high degree of the conversion, after the access to the material of the ambient air has been stopped. Investigations of the polymerization kinetics of irradiation and at various temperatures, indicated that, in the first degree of approximation, the process by its character is identical to polymerization process of peroxide type and another types of radical polymerization. On opinion of the authors of the paper cited, the polymerization process is initiated by products of radiation chemical oxidation of methyl methacrylate (probably peroxides formed by interac-

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tion of primary free radicals with oxygen). Being high active these products create possibility the low-temperature polymerization to be executed. The feature of interest is the fact the curves representing polymerization kinetics are in this case more smooth in comparison with those in the case of polymerization by benzoyl peroxide. The "gel-effect" in the processes described take place when a considerably more high degree of conversion is achieved and the ratio of the maximum reaction rate in the self-acceleration stage to the initial rate is of smaller value. The curves representing the dependence of ratio of polymerization rate in a given moment to the initial rate upon relative duration of the process are shown in Fig. 9.

Recently the paper of S.S. Medvedev, A.D. Abkin with collab. MS about polymerization of ethylene under γ -radiation Co^{60} was published. In this work the rate of radiation polymerization of ethylene in solution and in gaseous phase under various pressures (concentrations), as well as some properties of polymers formed have been examined. At a pressure 50 atm., temperature 25°C and dose rate 98 roentgen/sec polymerization of ethylene in heptane, cyclohexane, methyl alcohol and acetone proceeds with a rate 10 times exceeding the rate of the polymerization in gaseous phase at the same pressure. [In carbon tetrachloride tetrachloroalkanes with various molecular weight are formed. At the initial stages the process proceeds with acceleration, further the rate of the process being constant. The rate of the process is proportional

1 - pre-irradiation
 2 - initial rate of polymerization
 3 - rate of polymerization in a given moment
 4 - relative duration of the process
 5 - initial rate of polymerization

to irradiation dose rate in the power 0.3, while the radiation yield is ~~inversely~~ proportional to the dose rate in the power 0.7. The resulting polyethylene possesses higher density ($0.945-0.975 \text{ g/cm}^3$) and crystallinity than the high pressure polyethylene. Tensile strength of the polyethylene prepared by radiation-chemical method differs little from that of the high pressure polyethylene.

Kh.S. Bagdasarian, V.V. Voevodsky et al. ¹³⁸ have carried out investigation of graft-polymerization with irradiated ~~ed out investigation of graft-polymerization with~~ irradiated tolfen. For elucidation of mechanism of the process a method of electron spin resonance has been employed.

Kh.U. Usmayev, U.N. Musaev, R.S. Tillaev ¹⁴⁴ have investigated the radiation chemical method of preparation graft copolymers in the systems polystyrene-acrylnitril and perchlorvinyl-acrylnitril. It has been observed in the case of polystyrene and acrylnitril that the reaction proceeds in a polystyrene film swollen in acrylnitril under radiation up to dose $1 \cdot 10^6 - 4 \cdot 10^6$ recontgon. Preparation of graft copolymers on the basis of perchlorvinyl and acrylnitril was accomplished by irradiation of a perchlorvinyl film (in presence of air) with the consequent treatment with acrylnitril.

As it has been mentioned, radiation polymerization in the most of cases proceeds by a free radical mechanism. However, recently it has been established that under certain conditions ^{for example} (e.g. at low temperature) polymerization under action of ionizing radiation can also proceed by carbonium-ion mechanism. Thus A.D. Abkin et al. ^{139, 141} have demon-

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Table 2

Monomer	Concentration of monomer, mol/l	Polymerization rate (mol/l $\cdot 10^5$)				in: in block
		ethyl chloride	dimethyl formamide	triethyl- amine		
Styrene	2.0	1.95	no polymerization			
Acryl- nitril	3.5	no poly- merization	0.97	0.67	0.21	

4.

Realize the carbonic mechanism of polymerization by the action of ionizing radiations.

Investigation of employment of ionizing radiation for preparation of inorganic polymers are begun by soviet scientists. Thus, V.I. Spitsyn et al.¹⁴⁵ have demonstrated the potential possibility of polymerization of phosphonitryl chloride under electron radiation. It is of interest that in this case polymerization proceeds only in presence of oxygen.

6. Effects of ionizing radiation on polymers

In the USSR first systematic investigations of effects of radiation on polymer materials were carried out by V.A. Kargin with collob.¹⁴⁶⁻¹⁴⁹ concerning, mainly, change of thermo-mechanical properties of irradiated materials. At present investigations in this field are being carried out by a number of soviet scientists, (S.S. Medvedev, B.L. Karpov, Ya.S. Lashkin, B.L. Tsotlin, H.A. Slevokhotova, A.B. Faubman).

V.L. Karpov et al.^{150, 151} studied effect of radiation on various polymer substances^{*}. They employed radiation of different kinds including α - and β -radiation of radon and products of its disintegration, γ -radiation of Co^{60} , fast electron beams, mixed irradiation of nuclear reactor. It was found that all polymers can be subdivided into two principal groups. The polymers of the first group are characterized by predominance of destruction processes, i.e. rupture of polymer chain. The polymers, in which under action

^{*} Researches in the field of radiation chemistry of polymers had been begun by V.L. Karpov in 1947.

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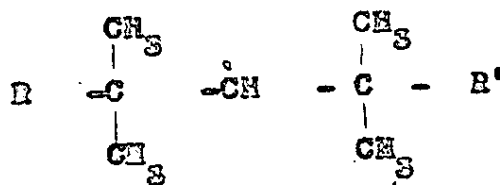
of radiation process of cross-linking predominates, i.e. formation of chemical bonds between macromolecules, constitute the second group.

the evolution of polymers under irradiation was studied by V.L.Karpev et al. ^{150, 152} and some conclusions concerning mechanism of radiation chemical reaction in polymers were deduced. In the case of cross-linking polymers the major part of gas evolved is hydrogen. [Thus for instance, under irradiation of polyethylene the gas evolved contains 93,5 % of hydrogen. This can be confirmation of the suggestion that the cross-linking process passes through intermediate stage of formation free radicals by rupture of C-H bonds. Destruction of polymers is observed in all the cases when the main chain of macromolecule contains quaternary carbon atoms. Under irradiation of such polymers the evolving gas is impoverished in hydrogen and contains considerable amount of compounds resulting from detaching of side groups at quaternary carbon atom.]

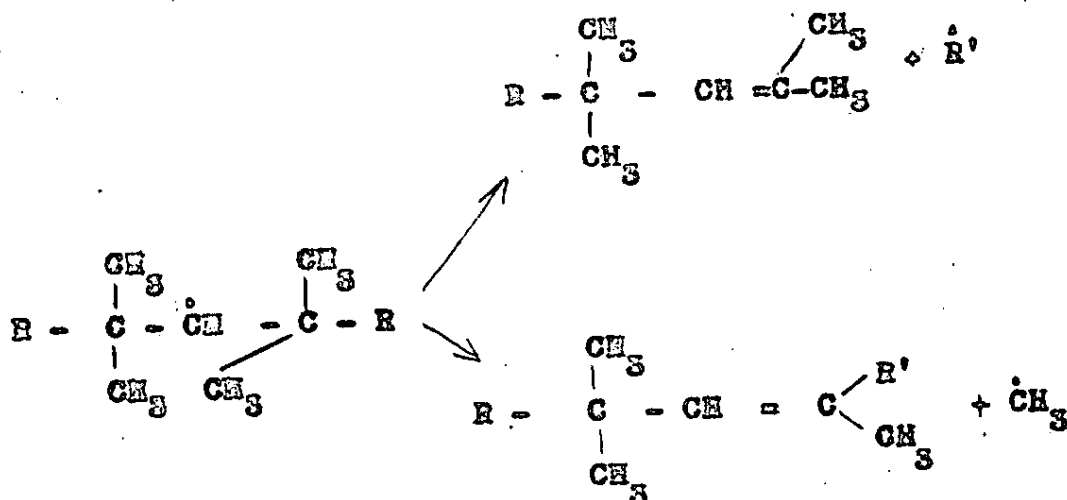
In their investigations V.L.Karpev and H.A.Slovezhetova ¹⁵³⁻¹⁵⁵ employed widely spectral methods. By this technique it has been found in the case of polyethylene that irradiation results in gradual disappearance of vinylidene double bonds, which were present in the original material in a little amount, and formation of new double bonds of the trans-vinyl type (mainly conjugated). Formation of the double bonds is also observed in the case of destructing polymers. [In polyisobutylene formation of double bonds precedes in all probability,

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by the following mechanism. By H-atom abstraction from secondary carbon atom the radical of the following type arises:



Because of steric hindrance this radical cannot form cross-link, and undergoes further destruction:



Irradiation of infra-red spectra has helped to discover the peculiarities of interaction of irradiation polymers with oxygen of the air. This process has been found to bring about formation of oxo-groups in the polymer. Another phenomenon of interest observed by V.L.Karpov et al.^{150,152,156} is destroying of crystallinity in polymers under effects of γ -radiation of Co^{60} or fast electrons. These processes were observed in the cases of polyethylene, guttapercha, co-polymer of vinyl chloride and vinylidene chloride, polytetrafluoroethylene and some other crystalline polymers.

V.L.Karpov, L.A.Blumenfeld et al.¹⁵⁷, by means of

measurements of infra-red spectra, absorption spectra and electron spin resonance spectra of irradiated polyvinylchloride have proved that the profound changes observed in this material under electron irradiation consist chiefly in splitting off hydrogen chloride and formation of double bond. On opinion of the authors, free radicals are responsible for change of colour in polyvinylchloride under effects of radiation. Their availability in the irradiated polymer has been proved by electron spin resonance method, their concentration being decreased with time progression. This decreasing is caused by recombination of the radicals in evacuated polymer and by interaction of the radicals with oxygen, resulting in formation of peroxide radicals if oxygen is available.

The papers of A.B.Taubman et al. ^{158,159} deal with problems of elucidating peculiarities of radiation destruction of polymers. They have examined the effects of electron radiation and high temperature on destruction of polytetrafluoroethylene, polymethylmethacrylate and polyethylene. The authors have obtained sharp change in rate of gas evolution under irradiation in narrow temperature region where melting (softening) of polymers is observed.

The phenomena of cross-linking in polymers are in focus of attention of soviet chemists since due to this process the most of polymers acquire the valuable properties. The mechanism of cross-linking in polyethylene has been examined by S.S.Medvedev et al. ^{160,161}. The temperature dependence of cross-linking in this material implies the cross-linking

being resulted by simultaneous detachment of two hydrogen atoms in a single primary act from two adjacent macromolecules.

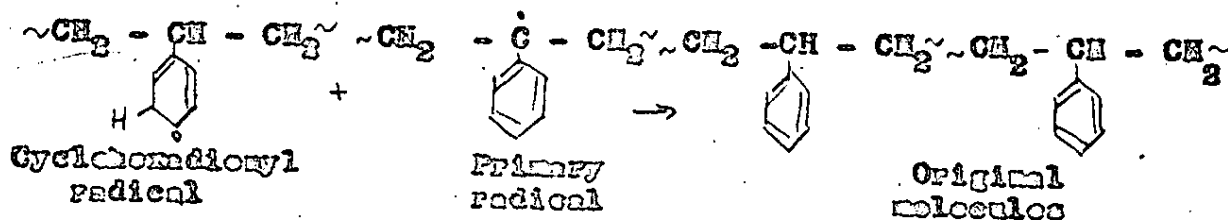
V.V.Voevodsky et al.¹⁶² have examined by means of ESR-method the formation of free radicals in irradiated polyethylene. Radicals of two kinds (of alkyl and allyl types) have been observed in irradiated polyethylene. The stability of those radicals is different implying the different mechanism of their recombination. On opinion of the authors the recombination of radicals accumulated in course of irradiation must play an important part in process of cross-linking in polyethylene.

In the recently published paper of S.S.Medvedev et al.¹⁶³ the conclusions of a considerable interest have been deduced concerning a protection effect mechanism of benzene rings in radiolysis of polystyrene. Polystyrene is known to have a high radiation stability: in the case of polyethylene formation of a single cross-link requires 25 - 35 e.v., while in the case of polystyrene 3000 - 6000 e.v. are necessary. Basing on investigations of radiolysis of toluene^o labelled by deuterium the authors have concluded that the high radiation stability of polystyrene is largely caused by disproportionation reaction of primary radicals with cyclohexadienyl

^o At the radiolysis of toluene the radicals formed have a structure similar to that of the radicals arising in polystyrene under irradiation.

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type radicals arising in the polymer under irradiation:



Yu. S. Lazurkin and G. P. Ushakov¹⁶⁴ have examined the radiation cross-linking of polydimethylsiloxane. The vulcanizates resulting demonstrate more high strength and resistance to freezing than that obtained by conventional methods. Radiation chemical cross-linking (vulcanization) of resins is an object of research of A. S. Kuzminsky, ~~V. L. Karpov~~ V. L. Karpov and T. S. Nikitina^{165, 166}. Radiation vulcanization of different resins has been established by the authors to can be a method of preparation of rubbers with new valuable properties.

S. A. Pavlova, S. R. Rafikov, B. L. Tsotlin¹⁶⁷ have obtained experimental evidence that the two opposite reactions, i.e. reaction of cross-linking and that of destruction under action of radiation on polyamides proceed simultaneously. [The authors have accomplished combined investigations including the change of mechanical properties, as well as the properties of the solutions, the change of molecular weight and molecular weight distribution function of the irradiated material. By this means they have succeeded in distinguishing of the two parallel reactions of cross-linking and destruction. Moreover, the cross-linking is a predominant process and vulcanization of polyamide is an final result of irradiation of this material.

Recent investigations of changes in the properties of

polymers immediately in the course of their irradiation accomplished by soviet scientists are of a considerable interest. Yu. S. Lazurkin et al.¹⁶⁸ have examined the change of mechanical properties of different polymers in the course of irradiation from nuclear reactor. Reversible radiation-mechanical effects have been observed to appear in the course of irradiation, i.e. change of mechanical properties appears in the time of irradiation and disappears after irradiation has been stopped. Reversible changes in gas-permeability of polymers in the time of γ -irradiation have been examined by V. L. Karpev et al.¹⁶⁹. It has been found that when the Co^{60} source of γ -radiation is put in or cut the rate of gas diffusion through the polymer undergoes a sharp change, approaching after irradiation the original value, but still remaining slightly higher than the latter.

Ya. M. Varchavsky, G. Ya. Vasiliev, V. L. Karpev, Yu. S. Lazurkin and I. Ya. Potrev¹⁷⁰ have studied isotope exchange between deuterium gas and different solid polymers in radiation field of a nuclear reactor to examine whether hydrogen from gaseous phase can be implanted into polymer molecules in course of irradiation. Polyethylene and polypropylene have been proved to trap the most amount of hydrogen in comparison with other polymers examined. The rate of isotope exchange is more slow in the case of polybutadiene and polystyrene. The authors have suggested that the intrusion of deuterium is caused by reaction of polymer radicals arising under irradiation and

-41-

donorium molecules:

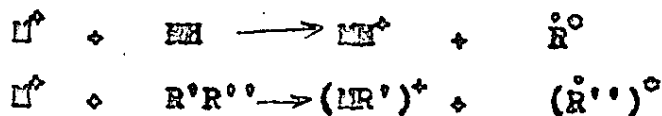


Use of isotope exchange technique in wide scale will, undoubtedly, assist to understand more completely the mechanism of polymer radiolysis.

7. Radiation elementary acts and primary chemical processes

In all chemical transformations in irradiated material secondary electrons, ions, excited molecules and free radicals (including atoms) are involved. The identification of these products is of a significant importance for elucidation of mechanism of radiation-chemical reactions. This problem is solved by means of mass spectrometry, electron spin resonance, etc.

V.L.Tal'roze and E.L.Frankovich¹⁷¹ employing mass spectrometry technique to investigation of products formed under electron impacts in some simple inorganic and organic compounds in gaseous phase, have found that the ion-molecule reactions playing an important part in primary radiation-chemical processes can give excited radicals:

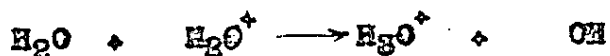
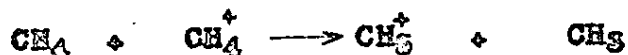


This phenomena has been observed in many processes in vapour phase [including $H_2^+ + H_2O \rightarrow H_3O^+ + H$; $CH_4^+ + H_2O \rightarrow H_3O^+ + CH_3$; $C_3H_8^+ + H_2O \rightarrow H_3O^+ + C_3H_7$, etc.]

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In another paper V.L.Tal'rose¹⁷² has pointed out that formation of different type traps under irradiation (especially in the case of hydrocarbons) can play an important part in radiation chemistry. Under irradiation of saturated hydrocarbons can arise unsaturated compounds and free radicals ionization potentials of which are lower than those of molecules of original substances. Such compounds and radicals can act as p- and n-traps. Increasing of amount of the traps in condensed phase creates the conditions which favour the principal elementary process consisting in recombination of "plus-minus" pair to be influenced with an adjacent free valence. One of two radicals arising at the recombination can add to this free valence, the probability of the latter process being, practically, equal to the unit in the case of hydrocarbon system.

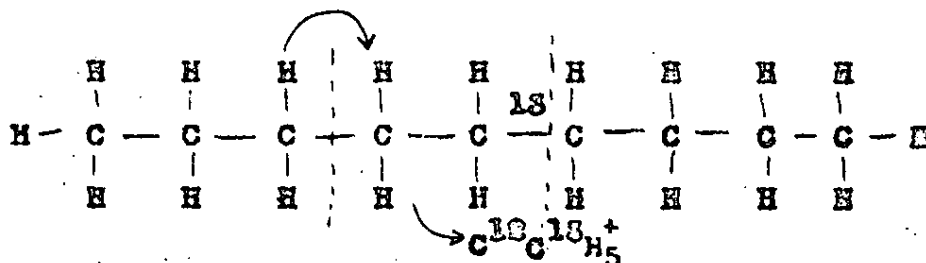
[Of great interest is employment of pulsed irradiation for measurement rate constants of ion-molecule reaction. Combining pulsed irradiation and mass spectrometry technique V.L.Tal'rose and E.L.Frankovich¹⁷³ have determined rate constants for the following reactions:



At 370° K the rate constant of the former is equal to $11.6 \cdot 10^{-11}$ cm³/mol.sec., that of the latter is $9.5 \cdot 10^{-10}$ cm³/mol.sec. at 410° K.

N.N.Tsitsky et al.¹⁷⁴⁻¹⁷⁸ are studying dissociation of rather large molecules under electron impacts using mass

spectrometry technique. Examination of mass spectra of halogenated hydrocarbons ¹⁷⁴⁻¹⁷⁵ indicated that with increasing of halogene atom quantity in the molecule the per cent of molecular ions in mass spectra decreases. The authors have also found ^{176,177} that the most complete agreement of calculated and experimental data take place when approximately equal probability of fragment ion formation from every part of molecule is supposed. For instance, in mass spectrum of n-octane-¹³C ions $C^{13}H_8^+$, $C^{12}C^{13}H_7^+$ and $C_2^{12}C^{13}H_7^+$ have been observed in amounts which are approximately equal to value which can be calculated proceeding from the assumption mentioned above. Based on analysis of mass spectra the authors have prepared the following scheme of large molecules dissociation:



Quite recently V.L.Tal'rose and E.L.Frankovich ¹⁷⁹ have carried out a comparative investigation of induced electrical conductivity and behaviour of free radical in irradiated solid paraffin. They have measured conductivity of paraffin irradiated at 77° K in the time of "annealing". In this case a sort of "flaring-up" of conductivity have been discovered (Fig. 10). This phenomenon appears as follows. At temperature differing by some dozens degree from the temperature region where "dark" conductivity take place, a considerable magnitude of conductivity is observed. A further increasing of tempera-

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ture the conductivity reduces to "dark" conductivity. The time-temperature ^{region} of "flaring-up" is coincident with the region where decreasing of ESR-signal is observed. Based on these data the conclusion has been deduced ^{according} to which formation of ions in irradiated solid or liquid material can proceed through formation of free radicals.

Fig. 10

V.V. Voevodsky et al 162, 180-185 are carrying out investigation of radicals appearing in radiolysis of organic and inorganic systems using electron spin resonance techniques.

The apparatus permitting the observation of ESR-spectra in the course of irradiation with fast electrons has been constructed by the authors 162, 180. By means of this apparatus ESR spectra and radical formation kinetics have been studied. The radicals forming under irradiation of teflon in vacuum at low temperature have been found to have a long life-time. In the air they convert peroxide radicals $-CF_2 - \overset{\cdot}{O} - CF_2 -$ which can be stored at room temperature for some 0 - 0.5 months.

In the case of benzene radicals C_6H_5 and C_6H_7 have been found to form 182,



In polyphenyls (diphenyl, p-ditolyl, etc) abstraction of H-atoms and CH_3 - groups situated in para-position with respect to phenyl substituent occurs to form a radical being analogous to C_6H_7 .

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✓ In this review we have not discussed some other branches of radiation chemistry developing in the USSR. This paper, for instance, does not contain any description of effects of ionizing radiation on catalysts and semi-conductors, neither does it contain chemical dosimetry or design of radiation sources. Nevertheless, the contents of the review gives an idea of the wide-scale work in the field of radiation chemistry carried out in the USSR.

There is no doubt that in the next years and decades more and more power radiation sources than at present will be available. Elementary particle acceleration technique is going to be improved day by day, power of nuclear reactors is also growing. It becomes then possible to obtain more and more highly active preparates of artificial radioactive isotopes. Energy released by uranium nucleus fission^{can}, undoubtedly, be used in future for new chemical processes to be put in practice. All these open bright perspective for radiation chemistry, which is one of the most progressive branches of modern physical chemistry and special chemical engineering.

Exchange of scientific successes achieved in this important field between scientists of different countries will promote the further progress of chemical science and its applications in interests of whole mankind.

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Captains to Photos

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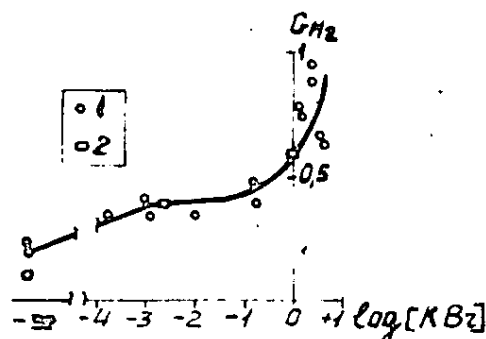


Fig. 1. The dependence of $G(H_2)$ on molar concentration of HBr solution under the action of protons with energy 660 Mev (1) and γ -radiation of Co^{60} (2)

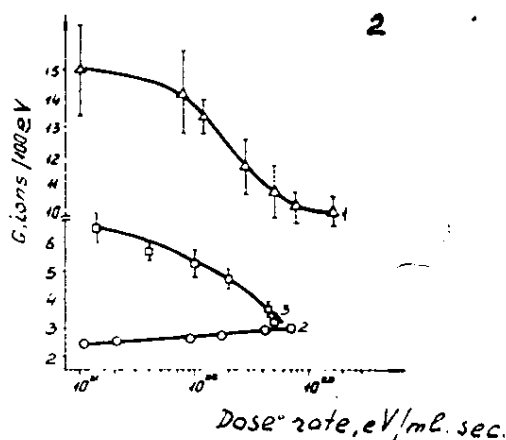


Fig. 2. The effect of high dose rates of radiation upon the yields of radiolytic transformations in aqueous 0.8 M sulfuric acid solutions:

- 1 - the dependence of $G(Fe^{++})$ on dose rate in $3 \cdot 10^{-3} M$ solution of ferrous ammonium sulfate;
- 2 - the dependence of $G(Ce^{++})$ on dose rate in $2 \cdot 10^{-4} M$ solution of ceric sulfate;
- 3 - the dependence of $G(Ce^{++})$ on dose rate in solution of the mixture of $Ce(SO_4)_2$ and $Tl_2 SO_4$ (concentration is $2 \cdot 10^{-4}$ and $1 \cdot 10^{-2}$ respectively)

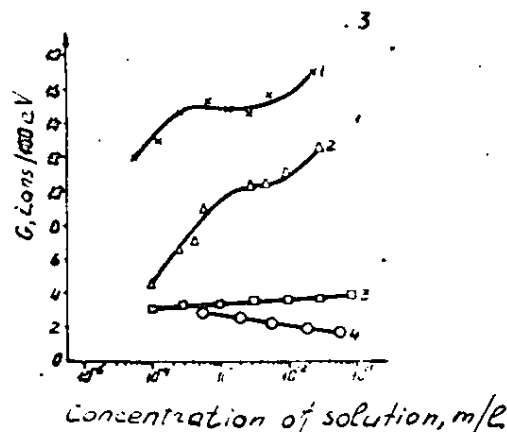


Fig.3. The dependence of the yields of radiolytic transformations on concentration of solution at high dose rates of radiation

1 - the effect of concentration of ferrous ammonium sulfate in aqueous 0.8 N sulfuric acid solution saturated with air on $G(\text{Fe}^{+++})$ at dose rate 10^{21} eV/ml. sec;

2 - the same at dose rate $3,5 \cdot 10^{22}$ eV/ml. sec;

3 - the effect of concentration of thallous sulfate in 0.8 N sulfuric acid solutions of the mixture of Co^{+++} and Tl^+ salts saturated with air on $G(\text{Co}^{+++})$ at dose rate $4,5 \cdot 10^{22}$ eV/ml. sec;

4 - the effect of concentration of cobrous sulfate in 0.8 N sulfuric acid solutions of the mixture of Co^{+++} and Co^{++} salts on $G(\text{Co}^{+++})$ at dose rate about $5 \cdot 10^{22}$ eV/ml. sec.

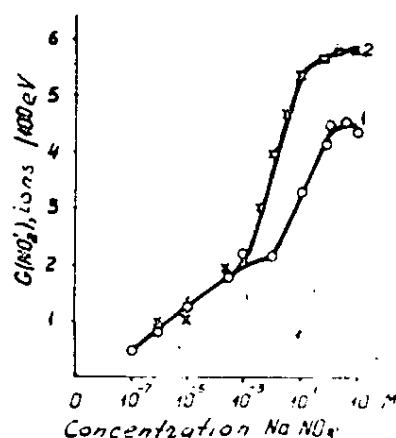


Fig.4. The dependence of $G(\text{NO}_3^-)$ on concentration of NaNO_3 in solution saturated with nitrogen ($\text{pH} \approx 14$):

1 - in absence of glycerol

2 - in presence of glycerol at 10^{-3} concentration.

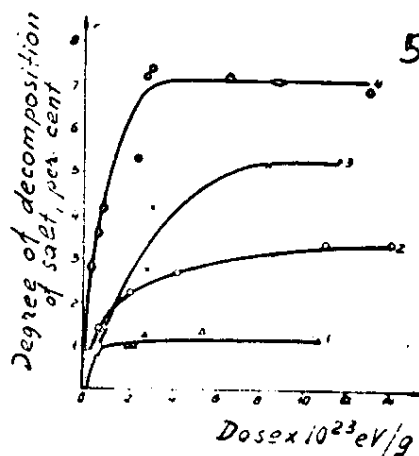


Fig.5. Decomposition of complex salts of platinum under the action of high energy electron beams depending on integral dose.

1 - $(\text{NH}_4)_2[\text{PtCl}_6]$

2 - $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$

3 - $\text{cis}-[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

4 - $\text{trans}-[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

Temperature of the experiments was $145-150^\circ \text{C}$.

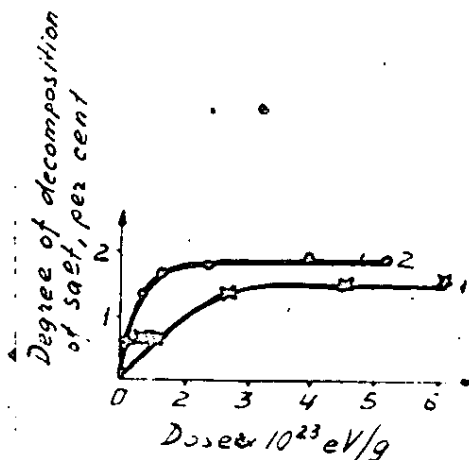


Fig.6. Decomposition of potassium chloroplatinate (1) and ammonium chloroplatinate (2) under the action of high energy electron beams. Temperature of the experiments was 20-95° C.

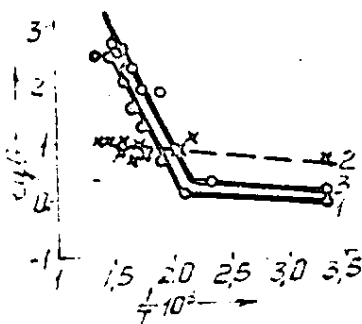


Fig.7. The dependence of logarithm of radiation-chemical yield of methane (1), hydrogen (2) and hydrocarbon fraction C_2-C_3 (3) on inverse temperature of the radiation thermal cracking.

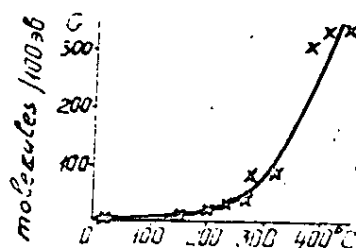


Fig. 8. The dependence of radiation-chemical yield of liquid olefins upon temperature of the radiation thermal cracking.

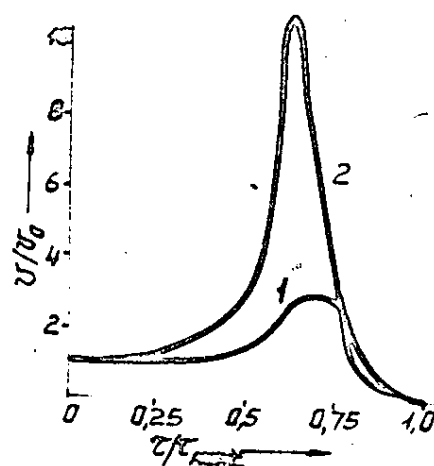


Fig. 9. The influence of a mode of initiation on the shape of the kinetics curves of polymerization of methyl methacrylate (temperature 60° C):

1 - polymerization of pre-irradiated monomer (dose $4 \cdot 10^{20}$ eV/cm^3)

2 - polymerization of methyl methacrylate in presence of benzoyl peroxide (0.01 %).

v/v_0 is the ratio of the polymerization rate in a given moment to the initial rate;

τ/τ_{max} is relative duration of polymerisation process.

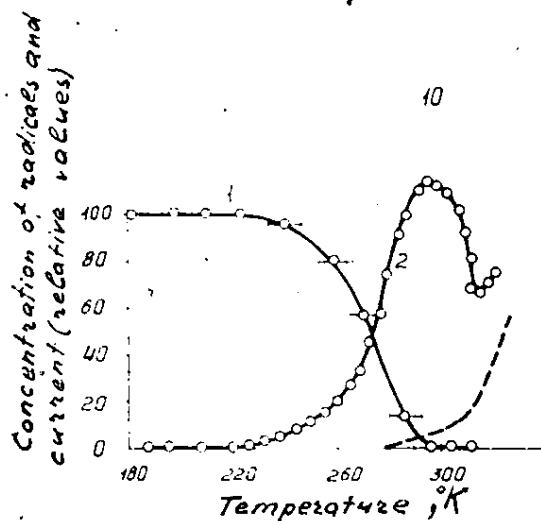


Fig. 10. Variation of radical concentration and electrical conductivity of irradiated paraffin under heating.

Heating rate is equal to $22^{\circ}\text{C}/\text{min}$.

- 1 - concentration of radicals (in arbitrary units)
- 2 - relative variation of the current through the sample at 1000 volts potential difference between the electrodes placed inside the sample. Variation of the dark conductivity is indicated with the dotted line.